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THE ABSORPTION SPECTRA OF CERTAIN SALTS OF COBALT, ERBIUM, NEODYMIUM AND URANIUM, AS AFFECTED BY TEMPERATURE AND BY CHEMICAL REAGENTS.

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[THIRTY-SECOND COMMUNICATION.]

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PART I.

Introduction.

The problems connected with the absorption and emission of light are of fundamental theoretical importance, and until they are solved we cannot claim any considerable knowledge concerning the structure of molecular and atomic systems, since light and heat radiations and absorptions are among the most characteristic properties of molecular and atomic structure. Although the conditions under which molecular and atomic systems absorb light are extremely complex and even yet are but partially understood, still many important facts are being discovered which increase our knowledge of molecular, atomic and interatomic structure.

[1] See Publication No. 130, Carnegie Institution of Washington.

Broadly speaking, the spectra of bodies can be divided into five kinds:

1. The first kind consists of a selective absorption and emission in which one or more ions or electrons for every molecule takes part. Examples of this kind of spectra are those of the organic dyes, and probably of many of the fluorescent and phosphorescent compounds of calcium, barium and strontium that have been investigated by Lenard and Klatt and others. These have been discussed in previous papers.[1]

2. The second kind of spectra consists of selective absorption and emission, which, in some cases, is made up of very fine bands. The vibrators in many cases (as indicated by the Zeeman effect which many of the bands show) seem to consist of electrons. The Zeeman effect is different and considerably more irregular than in the case of spark and arc lines. In some cases the Zeeman effect is of the same sign as that given by a positive electron. Only one electron or ion for every 100 to 10,000 molecules takes part in the absorption. Examples of this kind of spectra are furnished by the praseodymium, neodymium and erbium salts in solution, and possibly also by the uranium and cobalt salts. In some respects the uranium spectra are very different from the others, and as few definite Zeeman effects have been obtained, it may be that the mechanism of the absorption of the uranium salts is quite different from that of erbium and neodymium. A full discussion of this type of spectra will be given in the second part of this paper.

3. The third kind of spectra are the banded spectra of gases. These consist of groups of extremely fine lines. The law of Deslandres holds for the wave-length distribution of these lines and bands throughout the spectrum. For this kind of spectra the number of electrons and the damping factors have not been determined. In the case of the banded spectra of the fluorides and chlorides of calcium, barium and strontium, Dufour has obtained Zeeman effects that indicate the

[1] Jones and Strong: THIS JOURNAL, **43**, 100 (1910). Strong: Chemical Constitution and the Absorption of Light, THIS JOURNAL, **44**, 85, 107.

possible presence of positive electrons. Wood has succeeded in dividing the complex fluorescent spectra of sodium into simple series of lines, each one of which is stimulated by monochromatic light of a definite wave length.

4. The fourth kind of spectra consists of the emission and absorption spectra of gases, so-called line spectra, for which series formulas are in many cases applicable. The Zeeman effects in many cases indicate the presence of negative electrons and for the normal triplet the mean value of $e/m = 1.775$ has been found. It is possible that one or more electrons, or a system of electrons, in each atom take part in the absorption, although at any one instant only a few atoms in the gas are absorbing or emitting. Stark, Füchtbauer and others believe that these spectra are due to some kind of electrical dissociation.

5. The fifth kind of spectra consists of general emission and seems to be due to metallic electrons—electrons that are more or less free to move between the atoms.

Only the first two kinds of spectra are of interest in the present investigation, and as the second kind will be discussed later, the first type will be considered here. Attention is called to the recent papers of Koenigsberger and Kilchling[1] in this connection.

The absorption and reflection of light by the aniline dyes has been treated by Helmholtz, Drude, Lorentz, Planck, Voigt, and others, in the discussion of their electromagnetic dispersion theories. It is found that the reflecting power for any wave length is greatly affected if an absorption band lies in the neighborhood. In the region of absorption the value of nx (n the refractive index, and x the coefficient of extinction) may range from 0.1 to 6, whereas at distances of 1μ or more from the maximum of absorption it is never greater than $1(10)^{-6}$.

Using the Reiff-Drude formula, Koenigsberger and Kilchling found the following values:

[1] Ann. Phys., **28**, 889, 925 (1909); **32**, 843, 867 (1910).

	e.m.	
Tetraiodfluorescein	$1.25(10)^7$ negative electrons	Maximum of absorption shifts $8\mu\mu$ to the red when heated to 77°.
Fuchsine	1.37 negative electrons	Shift, $17\mu\mu$.
Cyanine	....	Shift, $6\mu\mu$.

COBALT SALTS.

Review of Previous Work.

Some of the most beautiful color changes known are those shown by solutions of cobalt and copper salts. For example, aqueous solutions of cobalt chloride are purplish red in color. When a concentrated aqueous solution of cobalt chloride is heated, or treated with hydrochloric acid, aluminium chloride, or calcium chloride, its color changes to blue, the change being quite sudden under certain conditions. On the other hand, the addition of zinc and mercury chlorides produces the reverse effect, changing the blue solution into a red one. Similar changes result when cobalt salts dissolved in other solvents are treated in the same way as aqueous solutions. A very considerable amount of work has been done on this subject by various workers and in general different theories have been offered to explain the results.

Russel,[1] Potilitzin,[2] Lescoeur,[3] Étard,[4] and others, favored the view that these color changes were due to the formation of different compounds of the cobalt salt with the solvent. The hexahydrate $CoCl_2.6H_2O$ is red, and when heated it is changed into the reddish lilac dihydrate, $CoCl_2.2H_2O$. When the latter compound is heated it is transformed into the dark violet monohydrate $CoCl_2.H_2O$. The anhydrous salt is blue and is formed at about 140° C. Étard showed that the solubility curve changed in direction at the tempera-

[1] P. Roy. Soc., **32**, 258 (1881). Chem. News, **59**, 93 (1889).
[2] Bull. soc. chim., [3] **6**, 264 (1891). Ber. d. chem. Ges., **17**, 276 (1884).
[3] Ann. chim. phys., [6] **19**, 547 (1890).
[4] Compt. rend., **113**, 699 (1891).

ture at which the red solution becomes blue. Charpy[1] showed the same to be true for the vapor tension-temperature curve.

Engel,[2] Donnan and Bassett [3] Donnan,[4] Moore,[5] and others do not believe that these color changes are solvation effects at all. Engel considers that double haloid salts may be formed. He points out that the blue anhydrous cobalt chloride becomes red when sufficiently cooled, and that the red anhydrous sulphate becomes violet when heated. Donnan and Bassett consider that the blue color of cobalt salts is due to the formation of complex anions containing cobalt. From boiling-point determinations they concluded that mercuric and cobalt chlorides in solution form compounds. When metallic ions of relatively strong basic properties like the alkaline earths or hydrogen are introduced with chlorine ions into a cobalt chloride solution, there is a formation of complex cobalt anions similar to those represented in the following schemes:

$$CoCl_2 + 2\overline{Cl} \rightleftarrows \overline{CoCl_4} \qquad CoCl_2 + \overline{Cl} \rightleftarrows \overline{CoCl_3}.$$

On the other hand, zinc, cadmium, mercury, antimony, tin, etc., form negative complexes more easily than cobalt, and hence they will cause the cobalt complexes to break up:

$$\overline{CoCl_4} \rightleftarrows CoCl_2 + 2\overline{Cl}, \qquad ZnCl_2 + 2Cl \rightleftarrows \overline{ZnCl_4}.$$

Vaillant[6] has made a quantitative comparison between dissociation and light absorption of certain electrolytes. In general, there is a close parallelism between these two phenomena. For concentrated solutions, however, there are marked differences which suggest the presence of other products than the simple salts and these Vaillant called hydrates. Pflüger[7] and Vaillant and Moore[8] have studied various salt solutions photometrically. They find the same absorption

[1] Compt. rend., **113,** 794 (1901).
[2] Bull. soc. chim., [3] **5,** 460 (1901).
[3] J. Chem. Soc., **81,** 942 (1902).
[4] Versuche über der Beziehung zwischen der elektrolytischen Dissoziation und der Lichtabsorption in Lösungen. Z. physik. Chem., **19,** 465–488 (1896); **53,** 317–320 (1905).
[5] Physic. Rev., **23,** 321, 357 (1906).
[6] Ann. chim. phys., [7] **28,** 213 (1903).
[7] Ann. Phys., [4] **12,** 1903.
[8] *Loc. cit.*

coefficients for dilute solutions of sodium, potassium, and barium permanganates, but for concentrated solutions they find differences. They conclude that absorption depends upon ionization.

A very detailed study of the effect of temperature on the absorption spectra of solutions has been made by Hartley.[1] He considered that the effect of change in temperature was largely due to change in the solvation of the dissolved salt. Bois and Elias[2] studied cobaltammonium sulphocyanate at 18° and —190° C. At the lower temperature the bands were smaller but were still very diffuse.

Uhler[3] has studied cobalt salts very systematically. Cobalt chloride in water was found to show rather fine bands at λ 6970, λ 6610, λ 6400 (weak), λ 6245 (weak), and λ 6095 (weak). In ethyl alcohol bands were found at λ 6950, λ 6360, λ 6150, and λ 6000.

Jones and Anderson[4] have made a detailed study of cobalt salts. Solutions of all the salts studied, except the sulphate, have a region of ultraviolet one-sided absorption. This they consider as due to association or solvation. In addition to the one-sided ultraviolet band, cobalt chloride has a band at λ 3300 which disappears very rapidly with dilution. This band they believe is due to some simple hydrate, and they consider that this simple hydrate is stable only in very concentrated solutions or at high temperatures. The green band appears for all aqueous solutions, and is independent of whether the cobalt exists as an ion, as a molecule, as an aggregate, or as a solvate, the absorbing power being apparently due to the cobalt atom. Absorption in the red is considered to be due to a simple solvate. In alcohol cobalt chloride has bands at λ 3100 and λ 3600, and also a green band. In methyl alcohol they find a fairly narrow band at λ 5910; one at λ 6050; a narrow intense band at λ 6240; a wide band at λ 6450; and a wide intense band at λ 6700. The position and

[1] Dub. Trans., [2] **7**, 253, 312 (1900).
[2] Ann. Phys., **12**, 262 (1908).
[3] Hydrates in Aqueous Solution, Carnegie Institution of Washington, Pub. No. 60.
[4] The Absorption Spectra of Solutions, Carnegie Institution of Washington, Pub. No. 110.

relative intensity of these bands are very different from that of the cobalt chloride water bands described by Uhler. In acetone broad bands appear at λ 5725, λ 6200, and λ 6780. These do not appear to be broken up into sharper bands under any conditions. By the addition of 5 per cent. of water to an ethyl alcohol solution of cobalt chloride, the water bands are made to appear, while for an acetone solution it requires the presence of at least 10 per cent. of water to bring out the water bands. Cobalt and calcium bromide in water are found to give bands at λ 6400, λ 6650, and λ 6950. Cobalt bromide in acetone has bands in the red that differ quite markedly from those of cobalt chloride in acetone.

Cobalt chloride in water (Böhlendorf).	Cobalt chloride in alcohol (Böhlendorf).	Cobalt chlorate in alcohol (Formánek).
λ 7100 to 6880	λ 7100 to 6570	λ 6850 to 6320
λ 6750 to 6530	....	....
λ 6400	λ 6400	....
λ 6260 to 6170	λ 6250 to 6170	λ 6245
λ 6070	λ 6070	λ 6058
λ 5610 to 4980	λ	λ 5906
		λ 5720
		λ 5265
		λ 5120

Rizzo[1] has investigated the effect of rise in temperature on the absorption bands of cobalt glass. He gives the following figures:

15°.	300°.	500°.
λ 6870 to λ 6380	λ 6900 to λ 6480	λ 6920 to λ 6460
λ 6030 to λ 5780	λ 6110 to λ 5800	λ 6130 to λ 5800
λ 5520	λ 5630	λ 5650

From the above summary it will be seen that our knowledge of the red cobalt bands is very limited at present. Much more work, similar to that on the uranyl bands described below, remains to be done. Apparently these cobalt bands are somewhat different from the uranyl bands; at any rate, the bands investigated by Bois and Elias did not break up into fine, sharp bands at very low temperatures.

In discussing the various spectrograms that show the effect

[1] Atti Torino, **26**, 632–638 (1891).

of change in temperature on the absorption spectra of salts, these spectra will be divided into three kinds:

The first kind of absorption consists of wide bands, in many cases hundreds of Angström units wide. In many of the spectrograms only one edge of the band may appear, the other edge of it lying in parts of the spectrum to which the photographic film is not sensitive, or to which the spectroscopic apparatus is not properly adapted. Examples of this kind of absorption are given by the copper or nickel salts, the ferricyanides, the chromates, etc. There is not the slightest indication of a finer structure to these bands.

The second kind of absorption spectra consists of diffuse bands that are quite narrow in many cases, and are usually very weak at ordinary temperatures. These bands may be from 10 to several hundred Angström units wide, and at very low temperatures may be broken up into finer and sharper bands. Examples of this kind of bands are the cobalt, uranyl, or uranous bands. In many cases these bands appear only under very special conditions of concentration and depth of cell. If the amount of absorbing material is large there is usually a wide absorption band in the region. This is well illustrated by the uranyl bands and the blue-violet band of the uranyl salts. If the amount of absorbing material is small the transmission of light is so great that these faint bands are entirely obliterated.

The third class of bands are sharp and appear over rather wide ranges of concentration. They are exemplified by the neodymium and erbium bands. This classification of bands is quite adequate for the present article on account of the salts studied and the temperatures used. It is very probable, however, that the latter two kinds of bands gradually merge into each other.

Glycerol Solutions of Cobalt Salts.

A dilute solution of cobalt chloride was placed in the silica cell and exposures were made at 10°, 100°, and 200° C. At 10° and 100° there was practically complete transmission throughout the visible portion of the spectrum. At 200° the whole shorter wave-length portion of the spectrum was

absorbed up to λ 6200. No indications of any fine bands in the red were to be noticed. A solution of normal cobalt bromide in glycerol was exposed in the same way as the chloride. There was practically no change in the absorption with rise in temperature. A more concentrated solution of cobalt bromide in glycerol was exposed in the silica cell at 10°, 100°, and 200°. At 10° there was a very diffuse absorption band extending from λ 5000 to λ 5300. At 100° this band had broadened so as to reach from λ 4900 to λ 5400. At 200° the whole of the spectrum of shorter wave length than λ 6200 was absorbed. No signs of the red bands appeared. Concentrated solutions of cobalt salts in glycerol become blue on being heated. Unfortunately the length of the silica cell prevented the use of concentrated solutions.

Summary.

It was found that glycerol solutions of the cobalt salts investigated do not show any of the fine red cobalt bands. Rise in temperature of the more concentrated solutions caused the yellow absorption band at λ 5100 to widen and to broaden out, so as finally to absorb all the red and thus cause the solution to appear blue.

Concentrated aqueous solutions of cobalt chloride show an enormous increase in the absorption with rise in temperature. Between quite narrow ranges of temperature there is a very great increase in the red absorption in the region of the finer bands. As the concentration is increased the temperature at which this great increase in the absorption takes place is lowered. For the more dilute solutions the widening of the absorption with rise in temperature is quite symmetrical.

The effect of rise in temperature on the absorption of cobalt nitrate and cobalt sulphate is quite small as compared with the effect on the chloride.

The presence of calcium or aluminium chloride with cobalt chloride in water increases the effect of temperature on the absorption, and causes the red absorption to take place in more dilute solutions than it does in pure cobalt chloride solutions. The temperature at which the absorption in the red increases so greatly may be called the "critical color temperature."

The "critical color temperature" seems to depend upon the existence of some *solvate* or *peculiar condition of the cobalt molecule*. The critical color temperature is much higher in water and glycerol than in other solvents. In a similar manner the water and glycerol bands are more persistent than the alcohol or acetone bands. It is important that a complete study be made of the critical color temperature for the various cobalt salts, and for the same salt in different solvents and when mixed with other salts. At the same time a study of the characteristic cobalt bands could be made.

A preliminary test was made to find if the presence of the NO_3 ion and water had the same hypsochromous effect[1] on the cobalt bands as it has on the uranyl bands. Unfortunately, no bands of any strength have as yet been detected for cobalt nitrate in water.

ERBIUM SALTS.

Of all compounds known, those of erbium probably show the most characteristic absorption spectra in the solid state and in solution. The first to make a detailed study of the erbium spectrum was H. Becquerel.[2] One of the minerals that he studied was xenotin or hussakite, a uniaxial crystalline compound consisting mainly of the phosphates of yttrium and erbium. The wave lengths of the ordinary and extraordinary spectrum bands are given. Becquerel found that the absorption spectrum observed in any direction through the crystal was made up by the superposition of two series of bands, one corresponding to vibrations normal to the axis of the crystal and the other to vibrations parallel to this axis.

Schulz[3] has worked on the effect of a magnetic field on the absorption spectrum (obtained by reflection) of erbium oxide. He finds that the bands $\lambda\lambda$ 4482.2, 4491.3, 4510.5, 4541.9, 4554.1, 4562.6, 4571.8, 4579.1, 4606.5, 4625.9, 5197.0, 5205.5, 5242.2, 5261.0, 5387.7, 6430.0, 6476, 6496, 6524, 6538, 6546, 6562, 6581, 6598, 6617 and 6652 broaden when the magnetic field is turned on; λ 4482.2 is shifted to the red; while λ 4510.5 and λ 4562.6 are shifted towards the violet.

[1] Strong: Physic. Review, **29**, 555 (1909).
[2] Ann. chim. phys., [6] **14**, 194 (1888).
[3] Astrophys. J., **30**, 383 (1909).

Bois and Elias[1] have made a very thorough study of the absorption of hussakite, erbium yttrium sulphate, erbium nitrate and erbium magnesium nitrate at 18° and at —190°, and also of the Zeeman effect at these temperatures. As the results are all collected in the above reference no detailed account is given here. In general, the bands show a Zeeman effect. Doublets and triplets are quite common.

A very extended investigation of the effect of low temperatures and magnetic fields on the absorption spectra of erbium has been made by J. Becquerel. As his papers are somewhat scattered, we give a rather full account of them. His first work[2] was upon the effect of a magnetic field on the absorption spectra of xenotin and tysonite at ordinary temperatures. In the following table + signifies a strong band and ++ a very strong band. Field always refers to the magnetic field which in this work is usually 14,100 c.g.s. units. Wave lengths are given in Angström units.

When the optic axis is parallel to the beam of light a crystal behaves like an isotropic body. When placed in a magnetic field, however, a rectilinear vibration is transformed into an elliptical one. This is Becquerel's magnetic double refraction. The effect of the magnetic field on vibrations normal to the field is different from the effect on vibrations parallel to the field. A crystal less than 1 mm. thick in a field of 2720 c.g.s. units causes a difference of $^1/_3\lambda$ in the middle of some bands.

To explain the Zeeman effect observed we must consider whether the external field is simply added to the intramolecular fields or whether there are variations produced there by the presence of the atoms. If we assume the same vibrators in every case, electrons with a value e/m of $1.8(10)^7$, then the internal magnetic fields must vary between 200,000 c.g.s. units in one direction and about the same number of units in the opposite direction. Assuming, on the other hand, that the external magnetic field is simply added to the intra-

[1] Ann. Phys., **27**, 279 (1908).

[2] Compt. rend., Mar. 26, Apr. 21, May 21, Nov. 19, Dec. 3, Dec. 10, Dec. 24, 1906; Jan. 21, 1907. Le Radium, Feb., 1907.

Xenotin.

Wave lengths.		I. Optic axis parallel to field.		II. Optic axis parallel to light beam.		III. Optic axis normal to field and light beam.[1]
Ordinary spectra.	Extraordinary spectra.	(*a*) Ordinary vibrations normal to the field.	(*b*) Extraordinary vibrations.	(*c*) Ordinary vibrations normal to the field.	(*d*) Ordinary vibrations parallel to the field.	(*e*) Extraordinary vibrations normal to the field.
5206.5++	.....	Doubles sym.		Doubles dis. sym. 3.1 A. U.	Spreads towards violet	
	5206.7++		Broadens unsym.			Doubles 3.7 unsym.
5211.3++	.....	Broadens sym.		Doubles	Broadens	
5215.5++	.....	Broadens sym.		Displaced to red	Doubles 3.7	
	5220.1++		Broadens unsym.			Broadens to red
5221.5++	.....	Doubles 5.9 sym.	Displaced 1.0 to violet	Displaced to violet		
5225.6	.....	Doubles 5.1 sym.		Displaced 1.0 to violet	Displaced to violet	
5236.6++	.....	Broadens sym.		Broadens	Doubles symmetrically	
	5237.2++		Broadens			Broadens
5242.0++	.....	Broadens sym.		Broadens	Broadens	
5245.8+	.....	Broadens		Doubles unsym.	Broadens	
5251.1	5251.1++	Doubles 2.6	Broadens	Doubles unsym.		Doubles unsym.
	5268.0+		Broadens			
	5388++ } 5394++ }		Doubles unsym.			Spread out towards violet
6422.7	.....	Doubles 8.9		No change		
	6424.6++		Broadens			
6434.5	.....	Doubles 7.7		No change		
	6435.8++		Doubles 9.8 unsym.			
	6463		Doubles unsym.			Broadens
6505.6+	6504.5	Doubles sym.		Doubles 3.8 unsym.	Spread towards violet	
6523.4++	6528.2	Doubles sym.		Doubles 4.4 unsym.	Spread 3.0 toward violet	
6537.0+	6538.0			Displaced 2.0 to red	Doubles 6.6 unsym.	Displaced to violet
	6542.8++		Doubles 4.7 sym.			Displaced to violet
6542.5	.....					
	6563		Displaced to violet			Broadens
	.....	Doubles 4.4 sym.		Doubles 4.6 unsym.		
6564.4+	6573.0++		Doubles 4.3 sym.			Spread out towards red
6571.6	.....	Displaced 1.7 to red			Displaced to violet	
6581.0+	.....	Broadens sym.		Weakened.	Spread out to violet.	

[1] Ordinary vibrations parallel to the field are the same as those under II*d*.

atomic field, Becquerel gives the following values of $e/m = 2\pi V \frac{d\lambda}{\lambda^2} \frac{1}{H}$, + referring to a positive electron:

	e/m.		e/m.
λ 5206.5^{++}	$+4.5(10)^7$	λ 5211.3^{++}	$-0.3(10)^7$
λ 5215.5^{++}	$+2.1(10)^7$	λ 5221.5^{++}	$+1.6(10)^8$
λ 5225.6	$-1.4(10)^8$	λ 5236.6^{++}	$+2.9(10)^7$
λ 5242.0^{++}	$+1.9(10)^7$	λ 5245.8^{++}	$+4.5(10)^7$
λ 5251.1	$-7.1(10)^7$	λ 6422.7	$-1.6(10)^8$
λ 6434.5	$-1.4(10)^8$	λ 6474.0	$+3.8(10)^7$
λ 6505.6^{+}	$+5.1(10)^7$	λ 6523.4^{++}	$-5.9(10)^7$
λ 6537.0^{+}	$-2.8(10)^7$	λ 6542.5	$+3.4(10)^7$
λ 6564.4^{+}	$-8.6(10)^7$	λ 6581.0^{+}	$+3.6(10)^7$

For convenience we will consider that some of the above bands are due to positive electrons, and some due to negative electrons, according to the value of e/m as calculated from the above formula.

The magnetic rotatory polarization is very closely related to the Zeeman effect, the positive and negative electrons behaving differently in this case also, the sense of the rotation being different for the positive and the negative electrons.

J. Becquerel[1] gives a theory explaining the magnetic optical effects which are observed in crystals. The general basis of his theory is somewhat similar to that of Voigt.[2] The electrons are considered to move along each coördinate axis independently. The three directions are considered to be the same for each electron and independent of the period of the exciting light. The form of the equations is then similar to those of a pendulum experiencing great frictional resistance. The theory as here developed explains some, but not all, of the different types of resolution found experimentally. As different results have been obtained, especially by Page,[3] the development given by Becquerel will not be considered in detail.

Later papers by Becqurel[4] deal with the effect of a magnetic field on the absorption spectra of certain crystals of

[1] Le Radium, March, 1907.

[2] Ann. Phys., **6**, 346 (1899); **6**, 784 (1901); **8**, 872 (1902).

[3] Trans. Camb. Phil. Soc., **20**, 291, 322.

[4] Compt. rend., Feb. 25, Mar. 25, May 13, June 17, Aug. 19, 1907. Le Radium; Sept., 1907.

xenotin, tysonite, parisite, monazite, apatite, and zircon at low temperatures. The bands in general are displaced towards the violet, especially for tysonite, as the temperature is lowered. Many changes of relative intensity occur and at low temperature the bands are invariably narrower and more intense.

For xenotin the following table is given:

Ordinary spectra.		Extraordinary spectra.	
λ at 25°.	Displacement between 25° and —188°.	λ at 25°.	Displacement between 25° and —188°.
5206.5	Doubled, 0.4 to violet	5206.7	0.4 to violet
5211.3	1.5 to violet	5220.1	1.5 to violet
5215.5	0.5 to violet		
5221.6	0.1 to violet		
5236.6	0.5 to red	5237.2	0.5 to red
5242.0	0.9 to red	5251.1	0.6 to red
5245.8	0.5 to red		
5251.1	0.6 to red	5268	0.4 to violet.

There does not seem to be any relation between the Zeeman effect and the effect due to change in temperature. Becquerel also states that the Zeeman effect is independent of the temperature. Related bands are usually affected in the same way by change in temperature.

The ordinary equation of an electron considered in the theory of dispersion is:

$$m\ddot{x} + \kappa\dot{x} + n^2x = eE \cos pt.$$

The resistance $\kappa\dot{x}$ designates a mean resistance, and causes the decay of the light vibration. It may result from sudden shocks undergone in any irregular or fortuitous manner by any of the electrons taking part in the absorption of light. The greater κ is the wider the band will be. The above equation leads to a value of the refractive index μ:

$$\mu^2(1-\kappa^2) = 1 + \Sigma \frac{e_h \partial^2(\partial^2 - \partial_{(h)}^2)}{(\partial^2 - \partial_{(h)}^2) + \partial^2 \partial_h'^2},$$

where κ is the coefficient of absorption; $2\pi\partial_{(h)}$ is the period corresponding to the middle of an absorption band h; e_h is a coefficient depending on the substance and the band, $e_h = \frac{4\pi V^2 e^2 / N_h \partial_{(h)}^2}{m_h}$; N_h is the number of electrons h/cc.; $\partial_h^1 =$

$\frac{\kappa_h}{m_h}\partial^2_{0A}$. Becquerel has obtained the value of the ratio of ∂^1 at 20° and at —186°. The bands are those of tysonite:

λ at 20°.	Ratio of ∂'.
4791 spec. extraord.	1.83
5176 spec. ord.	1.84
5235 spec. ord.	1.83
5825 spec. ord.	1.85

The ratios of ∂' are very nearly the same as the ratios of the square roots of the absolute temperature. The width of the bands measured between the maxima of the deviations of the dispersion curve vary directly as the square root of the absolute temperature.

If this law is true, then the size of the bands is proportional to the mean speed of translation of the molecules. Schönrock[1] has shown that the width of bands in a gas results not only from the Döppler effect due to the kinetic motion of the gas molecules, but also from collisions. Collisions determine the sudden and fortuitous variations in the phase, amplitude, and direction of motion of the electrons, and prevent the light that is being emitted or absorbed from being homogeneous. The size of the bands is then a function of the mean length of the wave trains emitted between collisions. If ∂ is the width of the band between the positions where the intensity of light is half the maximum, and r is the length of the train of waves emitted between collisions, then

$$\partial = \frac{1.39\lambda_0^2}{\pi r} = \frac{1.39\lambda_0^2 u}{\pi v L} = A\frac{\lambda_0^2}{L}\sqrt{\frac{T}{M}},$$

where u is the mean period of translation, L the mean free path, v the velocity of light, A is a constant, M the molecular weight, T the absolute temperature, $L = l_2/\rho^2\sqrt{2\pi}$, l is the mean distance between the centers of molecules, ρ is the distance between two molecules at the time of their collision.

If the temperature of the same mass and volume of a vapor is raised, l and ρ are but slightly changed, so that the width of the bands should vary as the square root of the absolute temperature. The above theory applies to a gas. The width

[1] Ann. Phys., **20**, 995 (1906); **22**, 210 (1907).

of the bands of solids cannot be explained on the Döppler-Fizean principle, but may be due to the extremely numerous shocks of the molecules. The fineness of the erbium bands may then be due to the union of several atoms into big molecules having a very small velocity of translation. If the molecules are large the collisions will be less numerous.

In a later paper Becquerel[1] gives some values for the terms which appear in his equation for determining the refractive index. It should be stated here that dispersion equations differ considerably according to the assumptions made in their calculation.

Tysonite.

λ at 25°.	lh at 25°.	lh at —188°.
4791	$2.29(10)^{-7}$	$7.23(10)^{-7}$
5176	$2.14(10)^{-7}$	$5.31(10)^{-7}$
5235	$0.71(10)^{-7}$	$1.53(19)^{-7}$
5825	$4.82(10)^{-7}$	$2.35(10)^{-7}$

From the changes of lh, the dielectric coefficient, with changes in temperature, Becquerel considers that the increase in intensity of the bands when the temperature is lowered is not only due to a narrowing of the bands, but also to an increase in the total amount of energy absorbed as the dielectric constant is increased. Let us assume that $e = 3.4(10)^{-10}$.

Tysonite.

	λ 5176.	λ 5235.
e/m	$+2.49(10)^{7}$	$-2.48(10)^{7}$
Ne at 25° U. E. M.	$1.01(10)^{-5}$	$3.28(10)^{-6}$
Ne at —188°	$2.50(10)^{-5}$	$7.07(10)^{-6}$
Nm at 25°	$4.05(10)^{-13}$	$1.32(10)^{-13}$
Nm at —188°	$1.00(10)^{-12}$	$2.85(10)^{-13}$
N at 25°	$0.89(10)^{15}$	$2.9\ (10)^{14}$
N at —188°	$2.21(10)^{15}$	$6.25(10)^{14}$

From the above, then, N, the number of absorbing electrons, increases as the temperature is lowered. The number of absorbing electrons is very much smaller than the number of atoms present. Hallo[2] and others have shown that only a small number of sodium atoms take part in the absorption of the two D lines:

[1] Le Radium, Nov., 1907.

[2] Arch. Néerlandaises, [2] **10**, 148 (1905).

D_2 (Hallo)	e_{0_2}	$=7.5\ (10)^{-8}$	N_{0_2}	$=3.3\ (10)^{14}$
D_1 (Gerst)	e_{0_1}	$=2.1\ (10)^{-7}$	N_{0_1}	$=1.1\ (10)^{15}$
λ 5221.5 (Xenotin)	$e_{25°}$	$=5.43(10)^{-8}$	$N_{25°}$	$=3.34(10)^{13}$
	$e_{-188°}$	$=9.68(10)^{-8}$	$N_{-188°}$	$=5.96(10)^{13}$

The index of refraction of solids, and especially minerals, changes very little with change in temperature, so that the electrons influencing refraction are but slightly affected by changes in temperature. Drude, Chéneveau,[1] and others, have shown that the number of these electrons vibrating in the ultraviolet is approximately that of the valencies of the atoms composing the molecule.

Becquerel[2] has continued his investigations at low temperatures, doing part of the work with Onnes[3] at Leyden. One of the problems arising from Becquerel's work is whether the paramagnetism of erbium and neodymium affects the internal magnetic fields which would exist within the crystals if they were diamagnetic. For this reason the Zeeman effect is found at widely different temperatures. If the Zeeman effect is independent of temperature then we should consider that paramagnetism did not play a very important rôle. Becquerel finds the Zeeman effect on the bands of xenotin and tysonite to be independent of the temperature.

In a table giving the Zeeman effect for tysonite and parisite it is seen that bands that are in practically the same portion of the spectrum are affected in a very different way by the magnetic field. From the Zeeman effect it is seen that the erbium alcohol bands λ 4870, λ 4880 and λ 5410 are due to negative, λ 5238 to positive electrons.

Considerable data are given by Becquerel upon the rotatory magnetic polarization. The results confirm the theory of the Hall effect—that the sense of the dispersion is just the opposite on the outside of the band to what it is on the inside. Applying the theory to the band λ 5221.5 of xenotin, Becquerel obtains the results shown in the following table:

[1] Le Radium, June, 1907.
[2] *Ibid.*, Jan., 1908; Nov., 1909. Compt. rend., Dec. 9, 30, 1907.
[3] *Ibid.*, Aug., 1908.

Temperature	H.	e/m.	N_e.	N_m.	N.
20°	14,100	$1.656(10)^8$	$3.78(10)^{-7}$	$2.28(10)^{-15}$	$3.34(10)^{13}$
—188°	12,300	$1.656(10)^8$	$6.74(10)^{-7}$	$4.07(10)^{-15}$	$5.96(10)^{13}$

Erbium Chloride in Glycerol.

Several photographs were made of the absorption spectra of erbium chloride dissolved in glycerol. The absorption is very similar to that of an aqueous solution, the bands, however, in general being shifted towards the red. The bands shown by a solution 30 mm. in depth are located as follows: λ 3250; λ 3370; λ 3510. These three bands are quite strong, being some 30 or 40 Angström units wide; λ 3600 is weak and narrow; λ 3650 is quite strong; λ 3785 is quite strong; λ 3885 is considerably weaker than the five other ultraviolet bands described above; λ 4165, λ 4490 and λ 4520 are of about equal intensity and quite strong (in the region near these bands there are numerous weak bands and these would come out better if a greater depth of cell could have been used, but on account of the slight solubility of erbium chloride in glycerol the use of a greater cell depth was not practicable); λ 4910 weak; λ 5190; λ 5210; λ 5225 rather strong; λ 5240 weak; λ 5260 weak; λ 5380; λ 5420; λ 5440; λ 6450; and λ 6530. The measurements were from a spark line at λ 3995 and hence are more accurate in this region. On the whole, most of the erbium chloride bands are of greater wave length for the glycerol solution than for the aqueous solution.

The relative intensities of the water and glycerol bands differ considerably, but the wave lengths do not appear to be very greatly changed. The photographic films appear to have contracted differently on drying, so that no very accurate comparisons of the wave lengths of the water and glycerol bands could be made.

Rise in temperature from 15° to 200° produces no noticeable change in wave length. At the higher temperature the bands are very much less distinct and apparently considerably weaker. For instance, the group of bands at λ 5200 at 15° practically becomes a single hazy band at 200°.

Absorption Spectra of Erbium Nitrate and Other Salts of Erbium.

It was thought to be of interest to test whether the NO_3 group had any hypsochromous effect on the absorption spectra of aqueous solutions of erbium salts. The following approximate wave lengths of the bands do not show any such hypsochromous effect as was found for the uranyl bands:

Erbium. nitrate.	Erbium chloride.	Erbium nitrate.	Erbium chloride.	Erbium nitrate.	Erbium. chloride.
3630	3635	4270[3]		5210	5205
3760[1]		4425	4415	5235	5230
3788[2]	3785	4480[4]		5363	5365
3880[3]		4500	4905	5420	5415
4045		4675[4]	4670[4]	6400	6410
4000		4730[4]		6480	6490
4160	4150	4850	4845	6530	6535
4100		4870	4865		
4215	4210	4910[4]	4905		

The crystals of erbium sulphate have fine absorption spectra. As the water of crystallization is driven off the bands change very considerably and become much more diffuse. The reflection spectra from fused erbium oxide consist of a large number of fine lines. As shown by Anderson, these lines become wider as the temperature is raised, until they become emission bands. The emission bands are quite broad. Between 100° and 600° some of the fine erbium bands shift about 10 Angström units. The difference between the wave lengths of the emission bands and the absorption bands at high temperatures, if it exists at all, is hidden by the haziness of the bands.

NEODYMIUM SALTS.

Introduction.

J. Becquerel has carried out investigations on several neodymium compounds similar to those on erbium. Tysonite was especially studied. This is a fluoride of cerium, lanthanum, and didymium and gives mainly the didymium spectrum. The bands $\lambda\lambda$ 5176++, 5234++, 6250 (doubles 4.5 unsym.),

[1] Hazy.
[2] Strong.
[3] Wide and weak.
[4] Weak.

6740, 6742+, and 6760+ were found to broaden in the magnetic field. Employing the usual theory of the Zeeman effect, Becquerel shows that λ 3995 is due to positive, λ 5075+ to positive, λ 5109+ to negative, λ 5176++ to positive, λ 5234++ to negative, and λ 7642+ to negative electrons.

At —180° the bands are much finer. The band λ 6249.7 is very fine and from the Zeeman effect it appears to be due to positive and negative electrons. The following table gives some of Becquerel's results.

The series of acetate bands is very much like that of the uranyl series, except that it runs in the opposite direction. The absorption spectra of uranous bromide in glycerol and in methyl alcohol are also similar.

Tysonite.

λ at —188°.		$\Delta\lambda H = 15000$.	$e/m = {}^2\pi v \frac{\Delta\lambda}{\partial H}$
3996	s	0.8	+ 6.3 (10)^7
4259.8	s and f	0.1	— 0.7 (10)^7
4268	s and f	0.1	+ 0.7 (10)^7
4721.4	s and f	0.1	— 0.6 (10)^7
5064.4	f	0.4	+ 2.0 (10)^7
5073.5	f	0.1	+ 5.32(10)^7
5079.1	f	0.54	— 2.63(10)^7
5087.2	f	0.99	— 4.81(10)^7
5098		0.33	+ 1.0 (10)^7
5110		0.92	— 4.4 (10)^7
5173	*s*	0.53	+ 2.5 (10)^7
5185.7	s and f	0.27	+ 1.26(10)^7
5220	s and f	0.14	— 0.64(10)^7
5234.6	s and f	0.54	— 2.48(10)^7
6224.9	f	0.4	+ 1.2 (10)^7
6234.8	f	0.5	— 1.6 (10)^7
6242.6	f	1.2	— 3.90(10)^7
6249.7	s and f	3.27	±10.52(10)^7
6267	f	0.4	+ 1.30(10)^7
6683		1.86	— 5.23(10)^7
6740		0.86	— 2.38(10)^7
6761		0.41	— 1.13(10)^7

Parisite.

λ at —188°.		$\Delta\lambda$.	e/m.
4274.8	*f*	0.20	— 1.38(10)^7
4724.7	*f*	0.42	+ 2.37(10)^7
4747.0		0.40	— 2.20(10)^7
5095.7	*s*	2.39	+11.56(10)^7
5186.0	*s*	0.37	+ 1.73(10)^7
5208.0	*s*	0.37	— 1.71(10)^7
5220.0	*s*	0.18	+ 0.83(10)^7
5231.0	*s*	0.27	+ 1.24(10)^7
5256.0		0.60	— 2.70(10)^7
5685.0		1.00	+ 3.90(10)^7
6232.7		0.77	— 2.40(10)^7
6239.6		1.14	— 3.70(10)^7
6246.9		0.60	— 1.90(10)^7
6723.0		0.90	— 2.50(10)^7
6735.0		0.90	— 2.50(10)^7
6746.0		0.90	— 2.50(10)^7

The above table shows that the Zeeman effect on related bands of tysonite and parisite is very different (parisite is a carbonate of the didymium group). An examination was

made of yellow Spanish apatite, a fluorphosphate of calcium and didymium. The apatite bands are quite broad. The band λ 5270 gave a circular vibration indicating positive, λ 5750 positive, λ 5820 positive, and λ 5860 negative electrons.

A solution of neodymium nitrate in ethyl alcohol has also been tried. The bands $\lambda\lambda$ 5229, 5219, and 5239 were broken into two components by the magnetic field, the amount being 0.5 Angström unit for H = 14,000 c.g.s. units. The sense of the polarization indicated negative electrons. The bands $\lambda\lambda$ 5815 and 5831 are affected but little and indicate positive electrons. The effect of the magnetic field seems to be independent of the solvent. The addition of perchloride of iron had no effect. The spectrum was observed as the solution was warmed so as to change the solid alcohol to liquid alcohol. No discontinuous change in the spectrum was noticed.

Neodymium chloride in alcohol (methyl) has a sensitive band at λ 5096, giving a separation of 1.1 Angström units for H = 14,000. The sense indicates a positive electron. The band λ 5207 gives a separation of 0.4 having a negative sense, λ 5220 a separation of 0.4 in a negative sense, while λ 5225 does not show any effect. The bands $\lambda\lambda$ 5761 (0.4, positive), 5787 (0.4, negative), 5796 (negative), and the two bands at 6800 (negative electrons) gave measurable Zeeman effects. No difference was found between "water" and "alcohol" bands.

The addition of small amounts of the nitrate of neodymium to the chloride in an alcoholic solution rapidly causes the disappearance of the bands $\lambda\lambda$ 5207, 5225, 5727, 5745, and 5761. When equal amounts of the two salts are present these bands have practically disappeared. The band λ 5220 remains. At the same time new bands appear at $\lambda\lambda$ 5235, 5777, 5814, and 6229. The band λ 5229 is due to negative, λ 5235 to negative, and λ 5814 to positive electrons.

Becquerel and Onnes[1] continued the work on absorption spectra at temperatures of liquid and solid hydrogen. The general effect of cooling is to make the bands more intense and often to cause new bands to appear. The reverse action

[1] Le Radium, Aug., 1908.

very seldom occurs. But when the temperatures of liquid hydrogen (20° absolute) or solid hydrogen (14° absolute)

	Stahl.	Demarçay.[1]	Muthmann.[2]	Drossbach.[3]	Foesling.[4]	Formánek.[5]	Exner.[6]
A	7420	7324	....	....	....	7291	....
B	6900	6910	6892	....	6895	6906	....
	6810	6804	6798	....	6775	6794	6750
	6710	6731	6720	....	6720	....	....
C	6360	6373	6360	....	6360	....	....
	6280	6292	6285	....	6278	....	....
	6240	....	6250	....	6254	6235	....
	6220	6234	6215	....	6217	....	....
	....	....	5834	....	....	....	....
	....	....	5808	....	....	....	....
D	5790	5783	5785	5880–5660	5788–5780	5797	5795
	5750	....	5754	....	5754	5759	5740
	....	....	5735	....	5735	....	....
	5720	....	5716	....	5716	....	....
	5330	5320	5323	5320	5323	5319	5235
	5240	....	5254	5270–5190	....	....	....
	5210	5220	5216	....	5216	5222	....
E	....	....	5205	....	5204	5209	....
	....	....	....	5160	....	....	5120
	5130	....	5120–5110	....	5124	5120	....
	5090	5109	5089	....	5087	5096	....

[1] Compt. rend., **126,** 1039 (1898).
[2] Ber. d. chem. Ges., **32,** (1899).
[3] *Ibid.*, **35,** 486 (1909).
[4] Z. anorg. Chem., **118** (1907).
[5] Die qualitat. Spectralanal. anorg. Körper, Berlin (1900).
[6] Sitzun. Wien., **118,** A, 1252–1266 (1899).

are reached it is found that many bands have weakened, or even disappeared. The band λ 5235 of tysonite is a band of

Table—(Continued).

	Stahl.	Demarçay[1].	Muthmann.[2]	Drossbach.[3]	Foesling.[4]	Formánek[5].	Exner.[6]
F	.....	.....	.....	4780	4799	4821	4830
	4760	4768	4745	.....	4748–4742	4759	4760
	4690	4691	.....	4710	4687	4695	4700
	4620	4624	4595	4630	4610	4614	4620
G	.....	.....	.....	.....	.....	4443	4430
	4340	4351	4340	4340	4330	4341	.....
	4280	4294	4325	.....	.....	.....	4270
	.....	4281	4273	4275	4271	4271	.....
	4190	4200	.....	.....	.....	.....	.....
J	3800	.....	3803	.....	3804	.....	.....
K	3560	.....	.....	3590	.....	.....	.....
	3540	.....	.....	3560	3538	.....	3478
	3500	.....	.....	3510	3503	.....	.....
	3470	.....	.....	.....	3468	.....	.....
L	.....	.....	.....	.....	3420	.....	.....
	3290	.....	.....	3370	.....	.....	.....
	.....	.....	.....	.....	.....	.....	3350–3130
M	3290	.....	.....	3280	.....	.....	.....

this kind. At very low temperatures, then, the spectrum is much simpler than at higher temperatures. Some of the bands even pass through a minimum of width. The band

λ 5176 of tysonite passes through a minimum between 20° and 14°. Becquerel suggests that there should be a relation between the effect of temperature on the absorption and on electrical resistance.[1] At very low temperatures the metals should be transparent.

The effect of a magnetic field on the absorption bands was found to be independent of the temperature, and this fact, Becquerel believes, is a strong argument for the view that positive electrons exist within the atoms.

The foregoing table gives the wave lengths of the neodymium bands in aqueous solution as measured by various spectroscopists:

Stahl states that the bands λ 6950, λ 6840, and λ 6780 vary enormously in their relative intensities in the various solutions. In the presence of strong nitric acid the bands λ 4710, λ 4690, and λ 4750 disappear completely. The absorption spectrum of the chloride is independent of the presence of free acid.

Neodymium: λ 6710, λ 6240, λ 5790, λ 5720, λ 4340, λ 4190, λ 3800, λ 3390, λ 3270.

Praseodymium: λ 5970, λ 5890, λ 4820, λ 4690, λ 4440.

The λ 4690 band is common to solutions of both neodymium and praseodymium, and this had led some to believe that there is a common element in these two substances. Stahl considers the view that there are several elements in neodymium as very improbable.

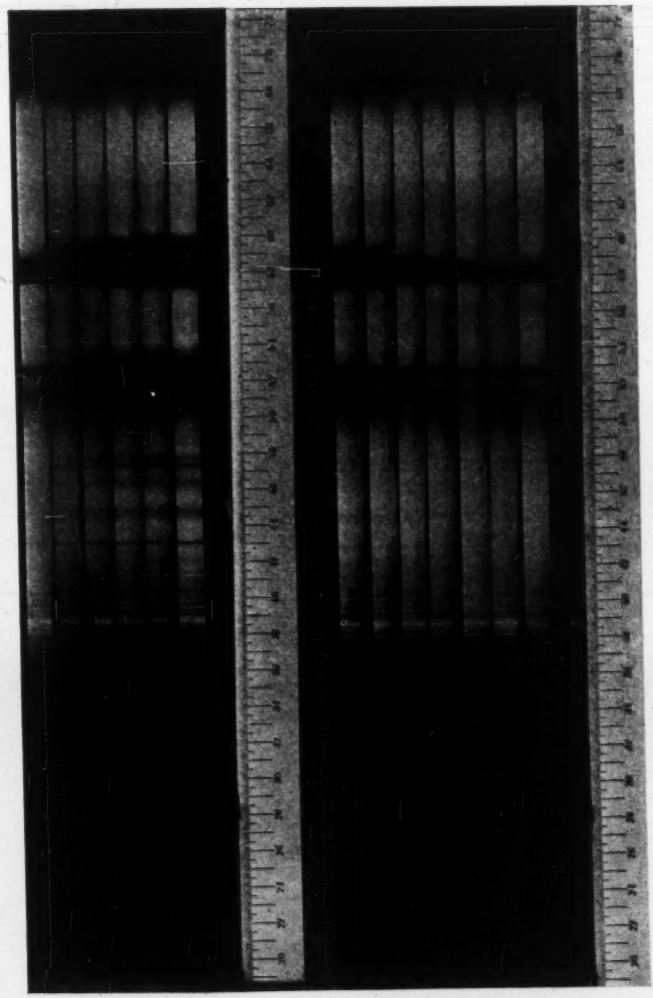
Neodymium Salts in Glycerol.

A run was made to test whether Beer's law holds for glycerol solutions. A spectrum was taken ranging from 0.84 to 0.105 normal, the amount of absorbing matter being kept constant. The more dilute solutions show greater general absorption in the ultraviolet. Otherwise Beer's law is found to hold.

Plate I, *A*, is the spectrogram of a solution of neodymium chloride in glycerol taken in the silica cell at various temperatures. The plate shows a slight widening of the bands, but this is very small. Some of the finer bands indicate a slight

[1] Onnes: Comm. Leyden. Suppl., **9**, 25 (1904); Onnes and Clay: Comm. Leyden. **95**, 99.

Plate I.



A B

shift towards the red with rise in temperature. This, however, is quite small and never amounts to more than 3 or 4 Angström units for any band.

A plate was made showing the effect of rise in temperature of solutions containing neodymium and aluminium or calcium chlorides in glycerol. In the third and fourth strips it is to be noticed that the wide band at λ 5800 is shifted slightly to the red. The band at about λ 4295 seems to be shifted 2 or 3 Angström units to the red. The shift is very small and is obscured in part by the increased diffuseness of the bands at the higher temperature.

The effect of rise in temperature on the absorption spectra of pure neodymium chloride in glycerol was studied. The shift of the bands in this case can hardly be noticed. The effect of the presence of calcium chloride is to cause the temperature shift of the bands to be increased. The effect is not as great as it is in aqueous solutions.

The absorption spectrum of neodymium chloride (Plate I, *A* and *B*) in glycerol is very similar to that of an aqueous solution. The ultraviolet bands $\lambda\lambda$ 3475 and 3550 are quite strong and sharp. A weak band appears at λ 3520. For the 3 mm. depth of cell and smallest concentration the following bands appear: $\lambda\lambda$ 4290 (weak), 4710 (very weak), 5120 (wide, hazy, and apparently a triplet), 5230, 5240 (strong and fairly sharp), 5250, 5270 (weak and fuzzy), 5740 (wide and hazy), 5790, 5805, 5820 and 5850. The latter three bands practically merge into a single band, the transmission between them being very weak.

The greatest concentration of the 9 mm. depth of cell (upper strip of Plate I, *A*) shows several additional bands: $\lambda\lambda$ 3600, 4190 (very diffuse), 4288 and two very fine components at 4270 and 4305, 4330, 4345, 4365, a wide (50 Angström units) band at 4460, and similar but weaker bands at 4620, 4840, 5340, 5940, 6240, 6265, 6400, 6800, with narrower and sharper bands at 4710, 4730, 4760, 4790, 5170, and 5190.

The "glycerol" bands are very similar to the "water" bands but are all of slightly greater wave lengths. The sharp "water" band at λ 4274 is composed of three bands in the gly-

cerol solution. The "glycerol" bands are quite persistent and for a solution containing 10 per cent. water the bands are practically "glycerol" bands. In general, the "water" and "glycerol" bands are so close to one another that we can not tell whether both bands coexist when the neodymium salt is dissolved in a mixture of the solvents. But the λ 4288 band apparently shifts gradually into the λ 4274 "water" band. No sign of the two bands coexisting is to be seen.[1]

Neodymium Nitrate in Nitric Acid.

Plate IV, *B*, shows the absorption spectra of neodymium nitrate in nitric acid. The effect of free nitric acid is very pronounced. All the bands are wide and diffuse and differ very much from the absorption when there is no free acid. The first band to appear is λ 5830 and shows as a very faint diffuse band. Then come the bands $\lambda\lambda$ 3470, 3520, 3550, 5130, 5250, 5730, 5970, and for a greater depth of cell $\lambda\lambda$ 4280, 4310, 4340, 4360, 4390 to 4460, 4480, 4600, 4650 (weak), 4705 (strong), 4745 (strong), 4840, 5385 (strong), 6245, 6275 and 6770.

In general, it has been shown that the effect of nitric acid is to shift the uranyl and uranous bands to the violet. This does not seem to be the effect of adding a large amount of acid to neodymium nitrate in aqueous solution. Many of the above bands do not seem to be bodily shifted to the red, but, like the band marked λ 4280, they are widened on the red side. The narrow band λ 4274 of the neutral nitrate lies within the broad and diffuse band λ 4280. As will be remembered, free nitric acid caused the uranyl nitrate bands to become sharper. At the same time the bands were shifted to the violet.

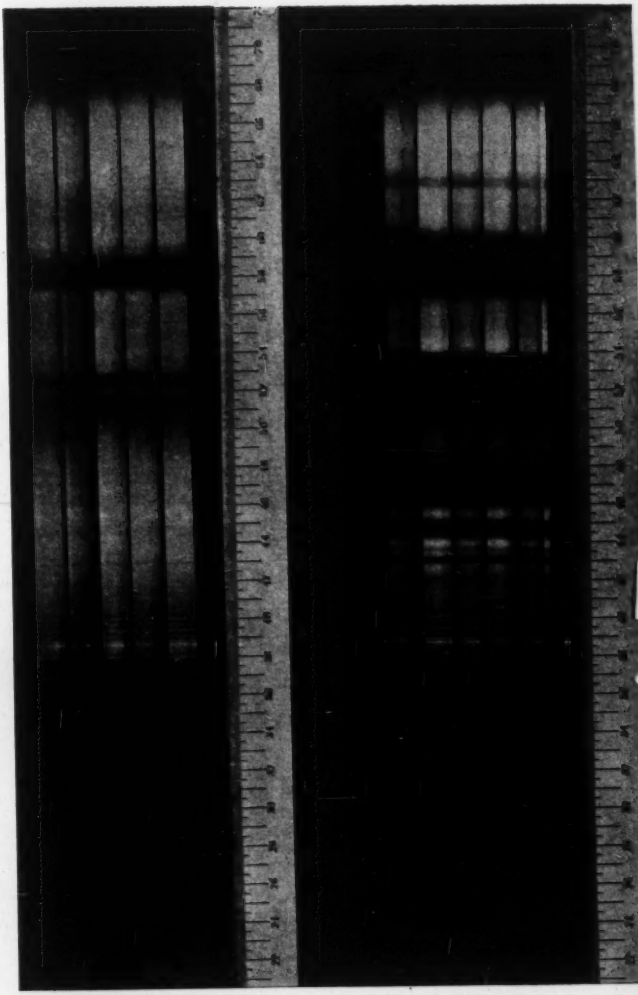
Some of the bands that Stahl considered as absent in the presence of nitric acid appear on our plates, the band 4705 above apparently being the same as his bands $\lambda\lambda$ 4690 and 4710.

Spectrophotography of Chemical Reactions.

During the progress of the work quite a number of photographs were made of a salt in mixtures of two solvents. It

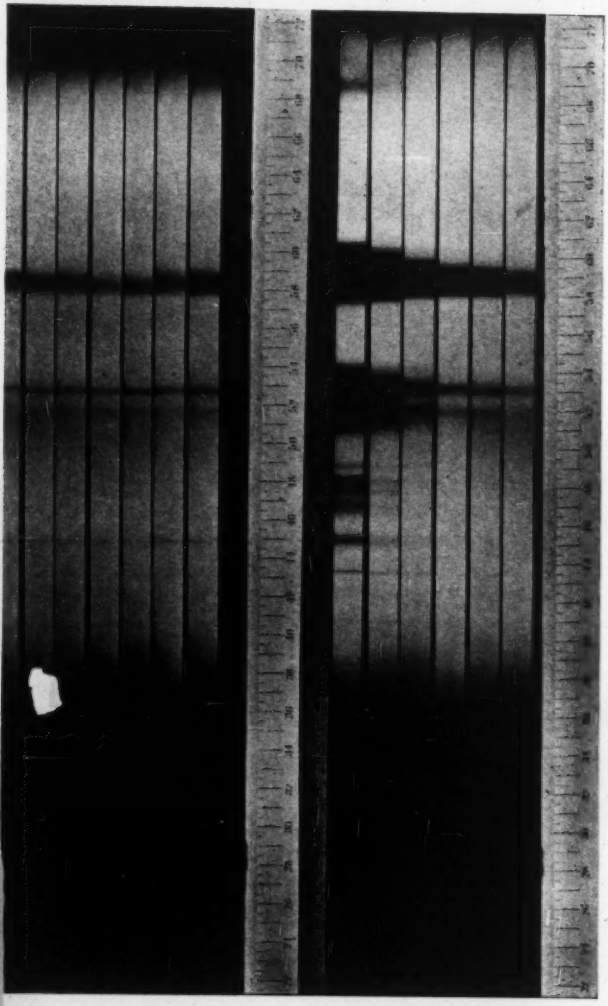
[1] For a detailed description of any plates not described in full in this paper see Publication 130 of the Carnegie Institution of Washington.

Plate II.



A B

Plate III.



A B

seemed of interest to photograph the absorption spectra of a salt when different amounts of an acid were added to the given salt in solution. *In the case of uranyl salts several were found to have different absorption spectra.* In the case of neodymium, however, it was found that the various salts had practically the same absorption spectra. The absorption of the acetate was, however, found to differ from that of the other salts, so that the chemical changes produced by adding various acids were photographed with the aid of the spectroscope.

Plate III, *B*, represents the absorption spectra of an aqueous solution of neodymium acetate, the concentration being kept constant and only the depth of cell being changed.

It will be seen from a mere glance that the absorption spectrum of the acetate is quite different from that of the other neodymium salts. All the bands are much wider and less intense. Many of the broad bands that appear as several finer bands in the spectra of the other salts appear here as single and very weak bands when the depth of cell is small.

The following are the wave lengths of a few of the bands: $\lambda\lambda$ 3485, 3520, 3820, 4040, 4200, 4295, 4333, 4360, 4460, 4630, 4720, 4770, 4850, 5140 (very wide and weak), 5260, 5360, 5660, 5800 to 5860, 6820, and 6950.

It will be noticed that all the bands are 10 to 20 Angström units farther to the red than the corresponding bands of the other neodymium salts.

Section *A*, of Plate III, represents the effect of adding nitric acid to a solution of neodymium acetate. The first strip of *A* represents a solution containing nitric acid and shows that the acetate bands have been shifted some 10 Angström units towards the violet by this addition of acid. This shift occurs before any other change of the acetate bands takes place.

Plate III, *A*, represents a spectrophotograph of the effect of adding nitric acid to an aqueous solution of neodymium acetate. The addition of nitric acid causes the absorption in the ultraviolet to increase. The general effect on the neodymium bands is to cause the bands to become sharper.

and, then, as more and more acid is added, to make the bands diffuse again. When the bands are sharpest they are practically the same as the bands of neodymium nitrate in water. It requires the addition of a very considerable amount of nitric acid to produce the nitrate neodymium bands.

The group of bands in the region λ 3500 in the first and seventh strips appears to be slightly displaced to the red. In fact, all the "nitrate" bands of the third and fourth strips are some 10 Angström units farther towards the violet than the bands of the first and seventh strips.

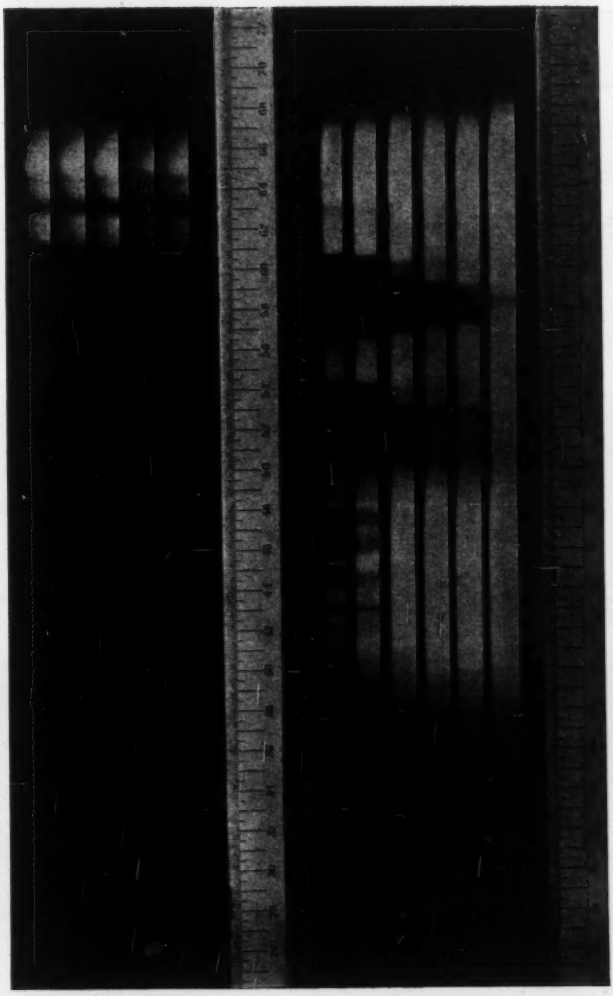
Strip 1.	Strip 3.	Strip 7.
3470	3465	3470
3510 very fuzzy	3505	3515 very fuzzy
3550	3533 sharp	3550
4285	3553	4285
4705	4275	4705
	4695	

In strip 1 there is a strong band at λ 5230 to λ 5250. In strip 2 appears a very fine and weak band on the shorter wave-length side of the white band at λ 5240. In strips 3 and 4 the two bands are of equal intensity and are located at λ 5225 and λ 5234. In strip 5 a band appears on the red side of λ 5234. At the same time λ 5234 has become very much stronger than λ 5225. In strip 7 λ 5225 has become very weak. In strip 7 there are weak and fine bands at λ 5205, and λ 5225, and a band from λ 5230 to λ 5250.

The group of bands at λ 5800 behaves in the same way. In strip 4 there are bands at $\lambda\lambda$ 5730, 5755, 5775, 5800, and 5820. In strip 1 is a hazy band at λ 5750 and others at $\lambda\lambda$ 5790, 5820, and 5870. In strip 7 there are four bands, two at λ 5730 to 5760 and two at λ 5770 to 5830. The bands $\lambda\lambda$ 6800, 7040, and 7100 appear only in the central strips.

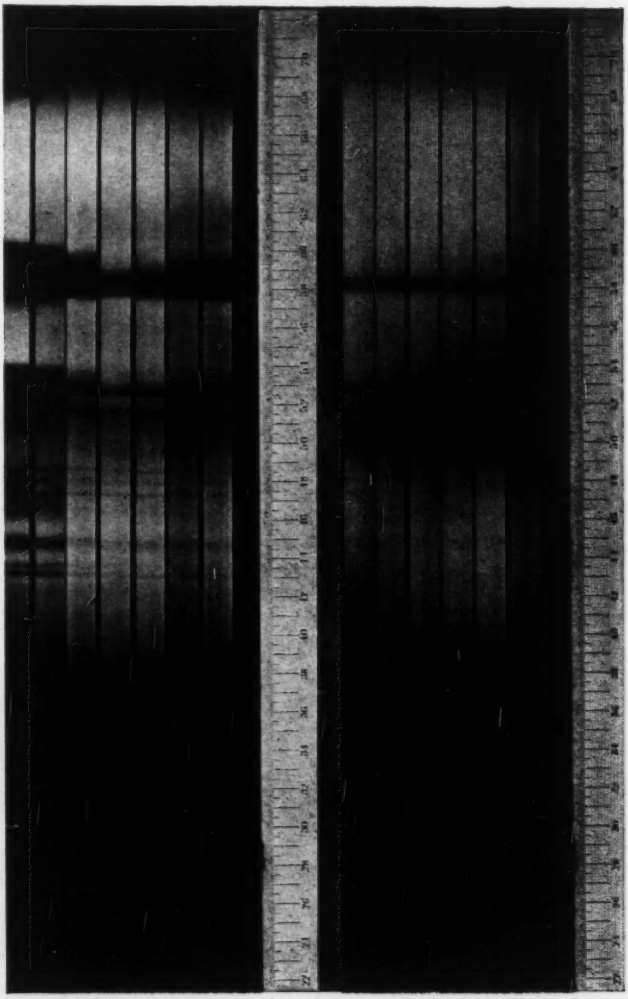
A spectrogram was made to show the coexistence of the "water" and "alcohol" bands of neodymium chloride. It is shown in Plate V, *A*. Anhydrous neodymium chloride was dissolved in a mixture containing 8 per cent. water and 92 per cent. ethyl alcohol. The first four strips represent a Beer's law run, the concentrations being 0.5, 0.3, 0.1 and 0.05 normal, the most concentrated solution being the one

Plate IV.



A B

Plate V.



A B

whose spectrum is next to the scale. The last three strips represent a constant concentration where the depth of cell is increased.

The spectrogram shows that Beer's law does not hold, the more concentrated solutions being the greater absorbers. This is especially true of the alcoholic portion of the absorption. In strip 1 the "alcoholic" band corresponding to the "water" band λ 4274 has about the same intensity as the "water" band. In strip 4, however, the "alcohol" band has become very weak, indeed, while the "water" band has slightly increased in absolute intensity as compared with strip 1. Several other bands indicate the same change. The "alcohol" bands thus weaken in intensity as the concentration is decreased, while the "water" bands do not.

In this connection experiments are now in progress in which it will be tested whether changes in temperature, the addition of chemical reagents, etc., affect the different bands in the same way.

Plate V, *B*, represents the effect of adding hydrobromic acid to an aqueous solution of neodymium acetate. The first strip represents the absorption of a solution of neodymium acetate in water to which about a drop of hydrobromic acid has been added. Strip 2 represents the same to which several more drops of hydrobromic acid have been added. The remaining strips represent the absorption of the same solution to which more and more hydrobromic has been added.

The first strip gives the characteristic acetate spectrum. In order to show the effect of the acid the wave lengths of the bands of the acetate measured on the film itself are given and compared with the spectrum of strip 2.

Strip 1.	Strip 2.	Strip 1.	Strip 2.
....	3465	4800 to 5150	4830
....	3510	gen. absorp.	5105
....	3543		5140
....	3560	5240	5225
4290	4285		5240
4450	4445	5745	5740
	4460	5760	5760
4715	4705	....	5775
4775	4775	5790	....
		5825	5810
		5870	....

The effect of adding a very small amount of hydrobromic acid is very pronounced. The addition of larger amounts of hydrobromic acid has very little effect. The shifting effect of hydrobromic acid is very small as compared with the same effect produced by nitric acid on the nitrate. The presence of a large amount of hydrobromic acid does not make the bands hazy and wide.

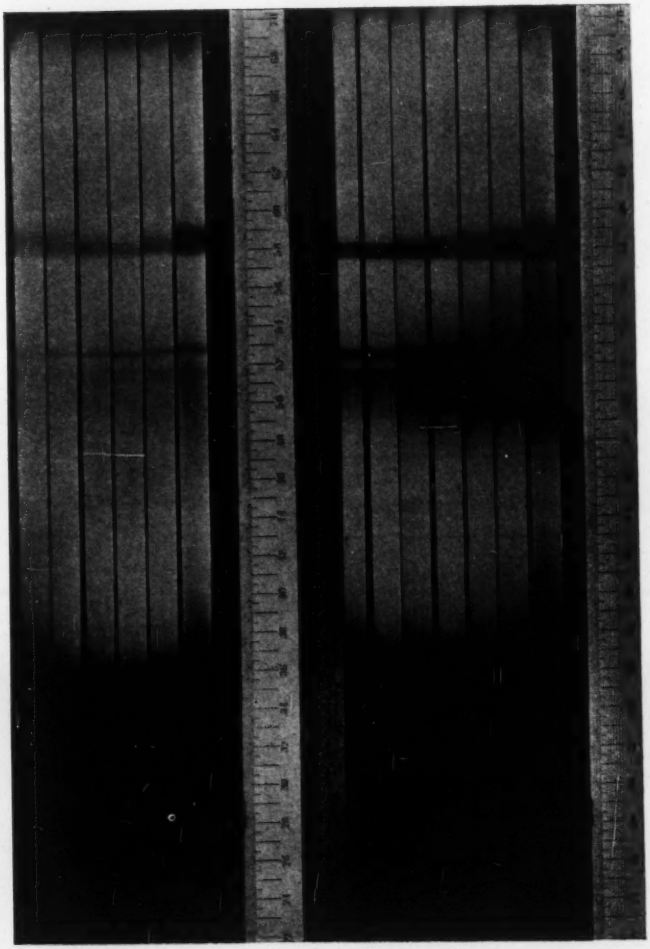
Plate VI, *A*, represents the effect of adding hydrochloric acid to an aqueous solution of neodymium acetate. The first strip represents the absorption of the pure aqueous solution of the acetate. The second strip represents the absorption of the same to which one drop of hydrochloric acid has been added. The third strip represents the absorption of the solution to which two more drops of acid have been added The acid used was concentrated. The following table represents in part the changes which the addition of acid has caused to take place.

It will be seen that the addition of but a small amount of acid caused the appearance of a large number of fine bands, especially in the region of λ 5800. It also caused a very considerable shift of all the bands to the violet, an action similar to that of nitric acid. Further addition of acid brought out a spectrum very similar to that of neodymium chloride as shown by strips 3 and 4. Still further addition of acid produces other changes, one being the appea ance of new bands in the region λ 5900.

Plate VII, *A*, gives a spectrogram where known amounts of hydrochloric acid were added to an aqueous solution of neodymium acetate.

Strip 1.	Strip 2.	Strip 3.	Strip 6.
3485	3465	3465(s)	
3530	3510	3510	The whole group is very weak and diffuse
3560	3540	3540 s	
....	3560	3560	
....	....	3580	
			4285 very weak
4297	4285	4285	5303 very weak
			5350 very weak

Plate VI.



A B

Table—(Continued).

Strip 1.	Strip 2.	Strip 3.	Strip 6.
	4710	4710	
	4775	4775	
	4845	4845	
5140	5110	....	
	5140	....	
	5225		
5260	5245	5230 s	5230 very weak
	5235	5245 s	5245 very weak
5760	5740	5740	5750
5810	5760	5760	5785
5850	5780	5780	....
	5795	5810	5815
	5815		5900
	5830		5930
	5865		
	5870		
	5895		
	5910		

A spectrogram (Plate VI, *B*) was made of mixtures in various proportions of neodymium acetate and neodymium chloride in water. Strip 1 is for the pure acetate and strip 7 for the pure chloride. The intermediate strip represents mixtures, the amount of chloride increasing from the bottom upwards. The concentration of neodym um was kept constant.

From this spectrogram evidence is obtained that each of the two salts has its own spectrum. As the amount of acetate is decreased the acetate bands gradually decrease in intensity and finally disappear. At the same time the chloride bands increase in intensity.

The band λ 5225 apparently is a chloride band, and does not appear in the acetate solution. On the other hand, the band λ 5830 and the very diffuse band λ 5860 appear to be acetate bands, and gradually disappear as the amount of acetate decreases.

A question which was raised by a study of some of the other spectrograms was whether by the addition of hydrochloric acid to the acetate different chemical compounds were formed. In the above spectrogram only two sets of bands appear,

and it thus seems very probable that when hydrochloric acid is added to the acetate more than two compounds exist, for there are more than two sets of bands. Indeed, it seems probable that there *is a whole series of compounds or systems formed between the acetate on the one hand and the chloride on the other.*

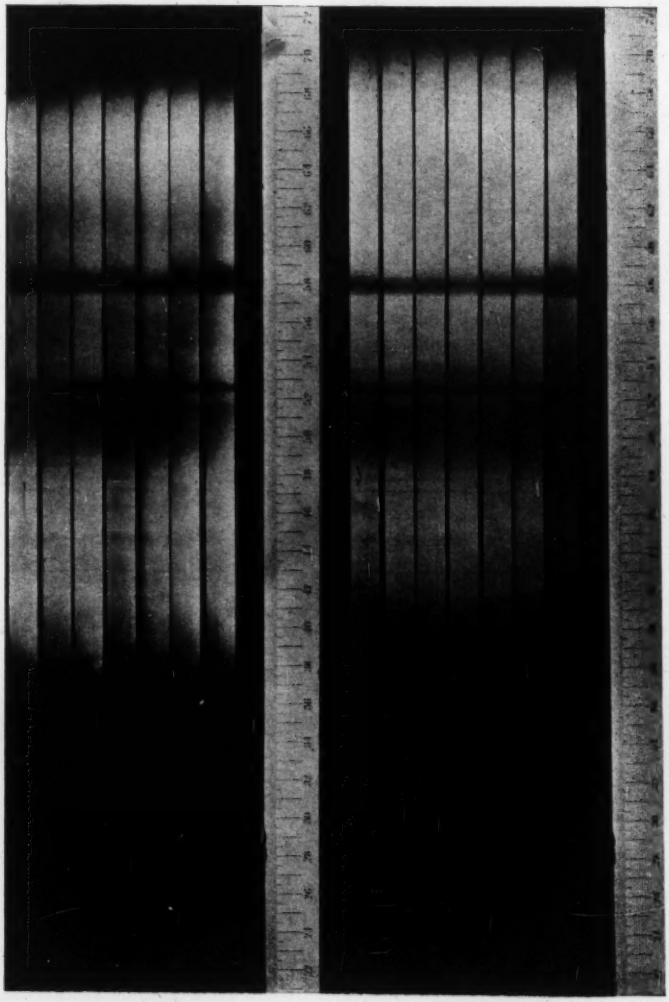
Plate VII, *B*, represents the effect of adding hydrochloric acid to an aqueous solution of neodymium citrate. The absorption spectrum of the citrate is very similar to that of the acetate, and the changes in the absorption spectra are very similar to those that take place when mixtures of the acetate and chloride are dissolved in water. In other words, there are bands here—"citrate" bands—which are very similar to the "acetate" bands. As hydrochloric acid is added the characteristic "citrate" bands gradually decrease in intensity while the "chloride" bands increase in intensity. There is no evidence here of more than two chemical compounds.

Summary.

No salts show the complexity of absorption spectra better than those of neodymium and erbium. Some of the bands are wide and diffuse, some narrow and strong—in fact, bands of very great diversity of appearance are present. In any given solvent the absorption spectra of the various salts are very similar and in many cases practically identical. But when the solutions are very concentrated or when the salts themselves are investigated, it is found that the absorption spectra are entirely different for each salt. The fact that the absorption of different salts in the same solvent is very similar is a strong argument *that the solvent plays a very important rôle in the absorption of light.* This view is very much strengthened when it is found that the absorption in different solvents is different, and that in mixtures of solvents both solvent bands coexist.

During the work on the absorption of uranyl nitrate to which sulphuric acid was added, the very fine banded absorption spectra of nitric oxide were obtained. From the conditions of the experiment it seems very probable that this nitric

Plate VII.



A B

oxide was in solution. Granting that this is the case, the experiment shows that the solvent itself under some conditions may not have any effect upon the absorption spectra. It seems reasonable to suppose that it is when chemical combination between solvent and solute takes place that the absorption of light is greatly modified.

In the case of neodymium bands it is very difficult to change the wave length of the bands. Becquerel and others show that there are small changes as the neodymium is cooled to very low temperatures. The absorption spectra of salts at 600° show but slight changes in wave length compared with the salts at 0°. For some bands the shift is about 10 Angs röm units. Our work shows practically no shift in the absorption bands of pure aqueous solutions between 0° and 90° C. However, when calcium or aluminium is present, in some cases there are shifts.

The absorption spectrum of neodymium chloride has been photographed in glycerol and alcohol solutions. There are indications of "alcohol" and "glycerol" bands. The latter are more persistent than the alcohol bands. In the case of glycerol there seemed to be one band that gradually shifted from the water to the glycerol position, indicating the possibility of the existence of intermediate glycerolates.

The effect of free nitric acid on the bands of neodymium nitrate is to cause them to become much broader and more diffuse than the bands of the neutral salt. Some of the bands are caused to broaden more on the red than on the violet side. The effect of free nitric acid on the neodymium bands is thus very different from the effect on the uranyl nitrate bands.

Early in the work it was intended to alter conditions so that each band could be followed throughout the various changes that it underwent. In most cases, however, this is at present very difficult to do, on account of the very sudden changes in the character of the spectra, and in many cases also on account of the diffuseness of the bands. For instance, the band λ 4274 is certainly one of the most characteristic bands of the water spectrum. In glycerol it is found that apparently this

band gradually shifts to λ 4288 for a pure glycerol solution. For solutions containing a large amount there appear fine satellites at λ 4270 and λ 4305. In alcohol the band appears at λ 4290. The band λ 4274 does not, however, shift into the alcohol band. In a solution of neodymium nitrate in water as made by Anderson there appear two strong bands close together, the distance between the opposite edges being about 10 Angström units, and between the adjacent edges, 2 Angström units. Neodymium nitrate and sulphate crystals each give two strong components, but in this case the distance between the opposite edges is 15 Angström units, and between the adjacent edges 6 Angström units. In other words, in the neodymium nitrate crystal the components are farther apart than in the nitrate solution as made by Anderson. In the solutions made by Jones only one component appears. A remarkable result manifests itself when the water of crystallization of the sulphate and nitrate crystals is driven off. The rather paradoxical effect is to cause the "λ 4274" bands to become weaker and appear as a single band. In the case of neodymium nitrate, driving off the water of crystallization causes many of the bands to be shifted towards the red. For the sulphate this drying results in a shift of some bands to the violet, while other bands remain unshifted. The dry nitrate bands in several photographs made by Anderson are all of some 50 Angström units greater wave length than the dry chloride, dry sulphate, or crystalline sulphate bands. It is at present premature to attempt to interpret these changes, since the intermediate steps have not been followed. Much work remains to be done in this direction.

In aqueous solutions it has been found that the absorption of neodymium acetate is different from that of the chloride, bromide and nitrate. Photographs have been obtained of the spectrum as the acetate was changed to another salt by the addition of inorganic acids. These spectra indicate that *in some of the reactions there probably exist several systems or compounds between the acetate and the salt of the acid added.*

Description of Plates I to VII.

Plate I. *A*. Neodymium Chloride in Glycerol. Cell depth constant, 9 mm.
Concentrations, 0.84, 0.63, 0.42, 0.28, 0.196 and 0.105 normal.

B. Neodymium Chloride in Glycerol. Cell depth constant, 3 mm.
Concentrations, 0.105, 0.143, 0.196, 0.28, 0.42 0.63 and 0.84 normal.

Plate II. *A*. Neodymium Chloride in Glycerol and Water. Cell depth, 2.2 mm.
Concentrations, 0.84, 0.80, 0.76, 0.67, 0.59 normal.
Percentages of water, 0.5, 10, 20, 30, 60, 90.

B. Neodymium Chloride in Glycerol and Water. Cell depth, 32.5 mm.
Concentrations, 0.59, 0.67, 0.76, 0.80, 0.84 normal.
Percentages of water, 90, 60, 30, 20, 10, 5 and 0.

Plate III. *A*. Neodymium Acetate to which Nitric Acid is Added. Cell depth, 30 mm.
Concentration of Neodymium Acetate, 0.041 normal.
Concentration of Nitric Acid, 0.117, 0.234, 0.585, 1.17, 4.09, 8.18 and 16.36 normal.

B. Neodymium Acetate in Water. Concentration, 0.041 normal.
Depth of cell, 1, 2, 3, 6, 14 and 34 mm.

Plate IV. *A*. Neodymium Chloride in Glycerol, 0.15 normal.
Temperatures, 20°, 60°, 110°, 150° and 180° C.

B. Neodymium Nitrate in Concentrated Nitric Acid. Concentration, 0.4 normal.
Depth of cell, 0.2, 0.8, 2, 6, 16 and 32 mm.

Plate V. *A*. Neodymium Chloride in Water and Ethyl Alcohol.
Solution contained 8 per cent. of water.
Strips 1, 2, 3, 4, Beer's law. Concentrations of neodymium chloride, 0.5, 0.3, 0.1 and 0.05 normal. Strips 5, 6, 7, concentration 0.5 normal.

B. Neodymium Acetate in Water. Strip 1 represents the neodymium acetate in water. Succeeding strips show the effect of adding more and more hydrobromic acid.

Plate VI. *A.* Neodymium Acetate in Water, 0.041 normal. Strip 1, pure aqueous solution. Strip 2, the same, to which one drop of hydrochloric acid has been added. Succeeding strips represent the addition of more and more hydrochloric acid.

B. Mixture of Neodymium Acetate and Neodymium Chloride in Water. Strip 1, all neodymium acetate. Strip 7, all neodymium chloride.

Plate VII. *A.* Neodymium Acetate in Water. Cell depth, 30 mm. Concentration of acetate, 0.041 normal. Concentration of hydrochloric acid, 0.113, 0.226, 0.566, 1.13, 3.95, 7.91 and 15.82 normal.

B. Neodymium Citrate in Water. Cell depth, 30 mm. Strip 2 and succeeding strips show the effect of the addition of hydrochloric acid.

(The second part of this article will appear in the February number of THIS JOURNAL.)

SELECTIVE OXIDATION.

BY HARRY C. JONES AND W. W. STRONG.

[THIRTY-THIRD COMMUNICATION.]

This is part of an investigation being carried out with the aid of a grant from the Carnegie Institution of Washington.

The power of solutions to absorb light enables us to distinguish between the parts of the dissolved salt combined with each solvent in a mixture of two solvents. If uranous bromide, obtained by the reduction of uranyl bromide with nascent hydrogen, is dissolved in a mixture of methyl alcohol and water we have two well-defined sets of absorption bands. One set is characteristic of the uranous salt dissolved in water and is what we term uranous "water bands." The other set is characteristic of the uranous salt dissolved in methyl alcohol, and we term these the uranous "methyl alcohol bands."

If we add certain oxidizing agents which are soluble in both water and methyl alcohol, the portion of the salt combined with water is oxidized and the part combined with

alcohol remains unchanged. This is shown by the fact that the "water bands" entirely disappear and the "alcohol bands" remain practically unchanged.

The experiment as actually carried out was the following: To two parts, by volume, of a solution of uranous bromide in water was added one part of water and six parts of methyl alcohol. The absorption spectra of this solution showed the bands of the "hydrated" uranous bromide and the bands of the "alcoholated" uranous bromide. A small amount of sodium perchlorate dissolved in methyl alcohol was added to the above solution. Sodium perchlorate is, of course, soluble in both methyl alcohol and water. There was usually a small amount of hydrobromic acid present from the reduction of the uranyl to the uranous salt. This would, of course, liberate perchloric acid which would be the real oxidizing agent. The result is that the uranous "water bands" disappear, showing that the uranous salt, bromide or perchlorate, had been oxidized to the uranyl condition. The "water bands" that disappear have the following wave lengths:

$$\lambda\ 4850,\ \lambda\ 4970,\ \lambda\ 5500,\ \lambda\ 6420,\ \lambda\ 6750.$$

The uranous "methyl alcohol" bands do not disappear, their intensities being practically the same as before the addition of sodium perchlorate. The more prominent of these bands have the following wave lengths:

$$\lambda\ 4900,\ \lambda\ 5020,\ \lambda\ 5260,\ \lambda\ 6220.$$

An experiment was carried out which was similar to the above, but in which a different oxidizing agent was used. Uranous bromide was dissolved in a mixture of methyl alcohol and water and calcium nitrate dissolved in methyl alcohol was added to the solution, calcium nitrate being soluble in both of the above solvents.

In this case the "water" bands disappeared entirely, and the intensity of the "alcohol" bands was not diminished in the least. These oxidizing agents, although soluble in both of the solvents present, are capable of oxidizing the part of the uranous salt that is combined with water—the hydrated

salt—but are incapable of oxidizing the part of the salt that is combined with alcohol—the alcoholated uranous salt. When hydrogen dioxide is used as the oxidizing agent, both the "hydrated" uranous bromide and the "alcoholated" uranous bromide are oxidized to the uranyl condition. Selective oxidation is shown by calcium nitrate and by sodium perchlorate, but not by hydrogen dioxide.

Similar results were obtained with uranous chloride. When calcium nitrate is added to a solution of uranous chloride in a mixture of water and methyl alcohol the "hydrated" uranous salt is oxidized and the "alcoholated" salt remains practically unchanged. When potassium chlorate is added to a solution of uranous chloride in a mixture of water and methyl alcohol, the absorption bands corresponding to the "hydrated" salt weaken very greatly in intensity, while the bands corresponding to the "alcoholated" salt do not show the slightest diminution in intensity. Potassium chlorate is only slightly soluble in methyl alcohol. Both the "hydrated" and "alcoholated" salt are completely oxidized by hydrogen dioxide.

The comparatively slow transformation of the "alcoholated" uranous salt into the "hydrated" salt is probably due to the presence of the uranyl ions in the water.

PHYSICAL CHEMICAL LABORATORY,
JOHNS HOPKINS UNIV., NOV., 1910.

THE ESTERIFICATION OF BENZAMIDE AND THE PREPARATION OF *N*-SUBSTITUTED BENZAMIDES.

BY E. EMMET REID.

Over fifty years ago, Kundig,[1] working in Kekulé's laboratory, noticed the production of ethylamine in a mixture containing alcohol and acetamide. Thirty years later, Bonz,[2] at the suggestion of Lothar Meyer, undertook a thorough study, quantitative as well as qualitative, of the reversible reaction

[1] Ann. Chem. (Liebig), **108**, 277 (1858).
[2] Z. physik. Chem., **2**, 865–900 (1888).

(1) $CH_3CO|NH_2 + H|OC_2H_5 \rightleftharpoons CH_3COOC_2H_5 + NH_3$.

In the reaction product he identified ethylamine, obtaining 0.343 gram of it from 10 grams of acetamide, and concluded that ethylacetamide was also present though he did not isolate it. He assumed that the amine was produced by the action of ammonia on the ester previously formed, thus:

(2) $CH_3COOR + NH_3 = CH_3COONH_3R$

He offered no evidence for this view but did show that the amine was produced immediately when alcohol was heated with pure acetamide. His results are more simply accounted for by supposing that the amide and alcohol react directly to form a *N*-substituted acetamide:

(3) $CH_3CONH|H + HO|C_2H_5 = CH_3CONHC_2H_5 + H_2O$.

He encountered great difficulties in estimating the amounts of amine and of substituted amide formed and practically gave up this part of the problem. A number of alcohols and aliphatic amides gave exactly similar results.

Romburgh,[1] Wheeler,[2] and many others have made substituted amides by the action of an acid chloride on the proper substituted amine.

Titherley[3] prepared a number of *N*-substituted amides by treating sodium amides with potassium alkyl sulphate.

In connection with a study of certain other equilibria,[4] I tried the action of alcohol on benzamide and, while the primary object was not attained any more than in the work of Bonz, yet ethylbenzamide was obtained so readily and in such quantity as to suggest this as a convenient method of preparing some, at least, of the alkylbenzamides. Further work has confirmed this supposition. The amines obtained as by-products are valuable and may be made the main object in the preparation.

[1] Rec. trav. chim., **4**, 388.
[2] This Journal, **21**, 190; **23**, 139, 142.
[3] J. Chem. Soc., **79**, 406.
[4] This Journal, **43**, 489; **44**, 76.

EXPERIMENTAL.

Benzamide (0.2739 gram) and 0.1840 gram of 100 per cent. alcohol, sealed up in a hard-glass tube, were heated 65 hours at 200° to 210°. The reaction product was a clear, homogeneous, thick liquid which did not solidify at —20°. The contents of the tube were poured into water and titrated with 0.1 N acid of which 1.18 cc. was required. Ethyl benzoate and ethylamine were recognized. The mixture was distilled with magnesium hydroxide into some of the same standard acid, and volatile base was obtained which neutralized 6.90 cc. After titration this was redistilled into pure hydrochloric acid and this evaporated to dryness by which process a crystalline residue was obtained which dissolved quickly and completely in 2 cc. of absolute alcohol and showed other properties of ethylamine hydrochloride. The ether extract of the alkaline residue from the first distillation yielded an oil which crystallized on rubbing and then melted at 65°.5–66°.2. The melting point of ethylbenzamide is variously given as 68°–69° and 71°. A single ether extraction of this same liquid, after acidifying, yielded enough benzoic acid to neutralize 5.00 cc. of 0.1 N alkali. Since the benzamide used was equivalent to 22.63 cc. of the standard acid, 1.18/22.63 or 5.27 per cent. of the amide had reacted with the alcohol according to equation (4):

$$(4)\quad C_6H_5CO\!:\!NH_2 + H\!:\!OC_2H_5 \rightleftarrows C_6H_5COOC_2H_5 + NH_3.$$

Since no benzamide was found, but in its place practically pure ethylbenzamide, reaction (5) must account for the other 94.73 per cent.:

$$(5)\quad C_6H_5CONH\!:\!H \qquad HO\!:\!C_2H_5 = C_6H_5CONHC_2H_5 + H_2O.$$

Supposing this to have gone to completion there would have been present in the tube 2.263 — 0.118 = 2.145 millimoles of ethylbenzamide and an equivalent amount of water. These would then react according to the reversible reaction (6), finally reaching equilibrium:

$$(6)\quad C_6H_5CONHC_2H_5 + H_2O \rightleftarrows C_6H_5COONH_3C_2H_5.$$

Equilibrium was reached when 26.7 per cent. of the amide has been transformed into the ethylammonium salt. For benzamide and water the limit was found at 25.2 per cent.[1] though the close agreement is accidental, since the limit very likely varies with the temperature as Menschutkin[2] found for aliphatic amides. The data for this sample and for five others which were heated at the same time with it but which were not analyzed for seven months after are given below in Table I. Some shifting of the equilibrium may have taken place in the interval. Though heated in the same tube, some of the samples were nearer the source of heat and were at a higher temperature than others, so it was to be expected that the limits would vary.

Table I. Benzamide and Ethyl Alcohol.

Benzamide, gram	0.2739	0.2836	0.3357	0.3189	0.3548	0.3063
Alcohol, "	0.1840	0.2153	0.1839	0.1704	0.1610	0.1572
Amide, millimoles	2.262	2.342	2.772	2.633	2.930	2.529
Alcohol millimoles	3.996	4.675	3.974	3.700	3.496	3.414
Ester, per cent	5.27	1.55	0.36	0.53	0.17	0.91
Hydrolysis, "	26.7	35.2	21.5	24.7	19.6	.....

In the first sample the titration of the reaction mixture was made with cochineal, which accounts for the high value obtained for the ester, since this indicator is not sufficiently sensitive to benzoic acid, changing color only for a considerable concentration of that acid. The titrations in the other cases were made with phenolphthalein. It will be noted that the amount of ester varies roughly with the excess of alcohol used in making the mixture. This is what would be expected, since whatever the course of the reaction at first, ultimately there will be equilibrium between the residual alcohol and the substituted benzamide on the one side and the ester and substituted amine on the other.

The reaction was next studied on a larger scale with a view to adapting it for use in the preparation of alkylbenzamides in quantity, but since the object was to determine the ultimate condition of things rather than to get the compounds easily and quickly, excessively long time periods were employed.

[1] THIS JOURNAL, **44**, 76.

[2] J. prakt. Chem., [2] **29**, 422–436, 445.

Since benzamide is very soluble in hot water while the alkylbenzamides are very sparingly soluble even in boiling water, benzamide can be readily extracted from the reaction product of an incomplete reaction and there is no practical need of pushing the reaction to the limit.

Since, in general, the equilibrium between an amide and water on the one side and the corresponding ammonium salt on the other shifts with change of temperature so that there is a higher percentage of amide at the higher temperature, it would be advantageous to use as high a temperature as practicable. In the present work, in which soft glass tubes were employed, the temperature was kept down on account of the rapid action of water on the glass at higher temperatures. Since there is no acid in the mixture there is no reason why an autoclave might not be used.

The benzamide was sealed up with a slight excess of alcohol in a large soft-glass tube and heated at 220°–230° for from two to seven days in the steel tube mentioned in a previous paper.[1] On opening the glass tubes, practically no pressure was ever found. The contents of a tube were poured into water and distilled with steam as long as appreciable amounts of ester passed over. The distillate was extracted twice with ether, the ethereal extract dried with calcium chloride, and evaporated at 100°, and the residue weighed as ester. The residue in the distilling flask was extracted twice with ether, the ether extract being washed with dilute acid, dilute sodium carbonate solution, and twice with water. The ether was evaporated at 100° or a little above and the residue weighed as alkylbenzamide. The aqueous portion was made alkaline and distilled into hydrochloric acid which was then evaporated to dryness and the residue after further drying at 120° was weighed. This was extracted with absolute alcohol and the residue dried and weighed as ammonium chloride. The difference of these two weights was considered the weight of the alkylamine hydrochloride present. The distillation residue was acidified, cooled to 0° and the benzoic acid filtered off, washed, dried

[1] This Journal, **43**, 489.

and weighed. The volume of the solution and washings was measured and the amount of benzoic acid remaining in solution calculated from its solubility (1.5 grams per 100 cc.) as given by Ost.[1]

The *N*-substituted benzamides remaining when their ether solutions were evaporated appeared as thick, colorless or slightly colored oils which solidified to solid masses of crystals. In the cases of the ethyl and propyl compounds, the solidification was rapid when once started and evolved considerable heat. Most of the data obtained are given below in Table II, but preceding that is a description of each experiment.

Experiment 1. Methyl Alcohol and Benzamide.—The mixture was heated for 69 hours at about 220°. When cool, the tube contained a thick, apparently homogeneous, slightly yellow liquid with a mere trace of thin rectangular plates suspended in it. After remaining liquid for nearly seven months, the contents of the tube solidified almost completely into a mass of thick transparent needles several inches in length. On pouring the mixture into water an acid, not an alkaline, mixture was obtained. All of the other experiments gave alkaline mixtures. In this case no attempt was made to obtain any ester. The methylbenzamide left on evaporation of the ether was pasty while all the others were solid. On pressing on paper, it gave a good melting point which was raised to 79°.8 by one crystallization from boiling water. Wheeler gives 80°–81° as its melting point.

Experiment 2. Ethyl Alcohol and Benzamide.—In this experiment the time was 68 hours and the temperature about 215°. The ester and amine were distilled off with magnesium hydroxide and steam, and the ethylbenzamide extracted from the distillation residue. The crude amide melted at 64°–66°.

Experiment 3. Ethyl Alcohol and Benzamide.—The alcohol used in this and in experiment 2 was of high purity and contained not more than 0.02–0.03 per cent. of water. The mixture in this case was heated 56 hours but on cooling, a considerable amount of transparent rectangular plates sepa-

[1] J. prakt. Chem., [2] **17**, 232.

rated. It was reheated for 70 hours at about 228°. The contents then appeared as a thick homogeneous liquid which solidified nearly completely to a mass of long, transparent, colorless needles. The 0.533 gram of ester obtained was distilled and began to go over at 210°, but the boiling point rose rapidly during the distillation, showing that the substance was not pure. The melting point of the crude amide was 58° and rose to 68°–68.°5 when the product was boiled with water and allowed to solidify. The amide is slightly soluble in boiling water. Such a solution filtered boiling hot deposited the amide as clear oily drops which on standing crystallized into a rosette of beautiful pure white needles, each one a hollow tube of square cross-section with square-cut ends. These were 10–12 mm. long and several mm. thick. From 360 cc. of the solution were deposited 3.68 grams o the amide melting at 68°.8. The hot saturated solution may, on cooling, become an emulsion from which the amide is slowly deposited in beautiful fine needles melting at 69°. The melting point is variously given in the literature at from 68° to 71°.

Experiment 4. Propyl Alcohol and Benzamide.—This mixture was heated for 72 hours at about 220°, but as on cooling, it contained crystals it was reheated for 70 hours longer at about the same temperature, though for a while it was as high as 250°. On cooling, it still contained crystals which were most likely propylbenzamide since no evidence of the presence of benzamide was found on working up the product. The 2.11 grams of ester isolated was distilled and about three fourths of it went over between 229° and 233°. The boiling point of propyl benzoate is 230°.7 and the substance was practically the pure ester. To get this ester, over 600 grams of water was distilled. The crude amide seemed to contain a slight amount of oil and without even pressing on paper melted at 62°. One treatment with boiling water raised the melting point to 76°. It is soluble in about 270 parts of boiling water. Such a solution when filtered and cooled gives a white emulsion. On standing several days the amide is usually transformed into beautiful, colorless, transparent, thin, square plates (melting at 83°), leaving the mother liquor per-

fectly clear. Titherley by a number of crystallizations from a succession of solvents raised the melting point to 84°.5.

Experiment 5. Isobutyl Alcohol with Benzamide.—The mixture was heated at irregular temperatures up to 230° for seven days. On cooling, the contents of the tube solidified to a pure white, fibrous mass. The 3.56 grams of ester obtained appeared to be impure for though it began to boil at about the right point, the temperature rose rapidly during the distillation. To get this ester over 1260 grams of water was distilled. The crude amide, without even pressing on paper, melted at 48°–49° instead of 57°–58°, which is the melting point given in the literature. Treatment with boiling water extracted 1 gram of benzamide and raised the melting point to 50°–52°. This amide dissolves into about 1300 parts of boiling water and on cooling gives an emulsion from which the amide is slowly deposited in short, thick needles melting at 56°. By adding about ten per cent. of alcohol, the solubility is greatly increased and well-formed colorless needles up to 30 mm. in length may be obtained. Some of these melted at 56°.5.

Experiment 6. Benzyl Alcohol and Benzamide.—A mixture of 2.85 grams of benzamide and 3.10 grams of benzyl alcohol was sealed up and heated for 70 hours at about 220°. The product was a yellowish solid. Carbon dioxide escaped in moderate quantity when the tube was opened. The product was extracted with ether and the ethereal soultion shaken with acid and alkali. It yielded a considerable amount of a flaky solid, melting at 95°–100°. This was crystallized from boiling water containing a little alcohol in which it is very slightly soluble and then melted at 104°.5. Benzylbenzamide melts at 105°–106°. Considerable benzoic acid, but no benzylamine, was isolated.

The upper portion of Table II gives actual weights in grams of the substances used and isolated while just below these quantities are given in moles.

Table II.

Number of experiment Alcohol used.	1. Methyl.	2. Ethyl.	3. Ethyl.	4. Propyl.	5. Isobutyl.
Benzamide, grams	24.52	28.99	26.88	30.38	24.60
Alcohol, grams	8.058	12.02	13.25	18.74	15.29
Alkylamide, grams	10.63	21.81	19.96	29.84	24.96
Benzoic acid, grams	12.57	8.11	10.23	6.98	4.75
Amine salt, grams	5.02	2.71	5.67	4.95	0.82
Ammonium chloride, grams	0.630	...	0.694	1.514	1.41
Ester, grams	...	0.298	0.533	2.11	2.92
Benzamide, moles	0.2018	0.2394	0.2220	0.2503	0.2031
Alcohol, moles	0.2515	0.2511	0.2877	0.3120	0.2061
Alkylamide, moles	0.0797	0.1464	0.1358	0.1829	0.1410
Benzoic acid, moles	0.1030	0.0671	0.0847	0.0573	0.0391
Amine, moles	0.0744	0.0324	0.0694	0.0502	0.0075
Ammonia, moles	0.0118	...	0.0130	0.0283	0.0264
Ester, moles	...	0.0020	0.0035	0.0129	0.0163
Benzamide accounted for	0.1827	0.2155	0.2240	0.2531	0.1964
Per cent. of benzamide accounted for	90.5	90.0	100.9	101.1	96.7
Yield of alkylamide, per cent.	39.0	61.1	62.6	72.9	69.4
Yield of ester, per cent.	...	1.27	1.58	5.2	8.3
Hydrolysis of amide, per cent.	61.0	38.1	36.4	23.1	24.3

It appears from these results that the yield of alkylbenzamide is satisfactory in all cases except with methyl alcohol where the hydrolysis was too great. In this case, however, ordinary methyl alcohol containing water was used. The sum of the equivalents of the amine and the ammonia should equal the sum of the benzoic acid and the ester. In all except experiment 5 there is a shortage of bases. There is some loss of bases in distilling their benzoates in getting over the ester. In case the action of the alcohol on the benzamide were entirely complete as represented below, the ammonia found should be equivalent to the ester. The excess of the ammonia found indicates that the reactions were not quite complete. By treating the isobutylbenzamide with boiling water 1 gram of benzamide was obtained. The equivalent 0.1410 given in the table for isobutylbenzamide should therefore be 0.1352 + 0.0083 = 0.1435. This makes the equivalent of benzamide accounted for 0.1989, raising the percentage from 96.7 to 97.9.

The amount of amide transformed into the ester increases, apparently, with the molecular weight of the alcohol. The difficulty with which the alkylbenzamide is formed seems to increase with the molecular weight of the alcohol.

Since, particularly in experiments 3 and 4, the products isolated and identified account very nearly for the amount of benzamide taken we may conclude that the action of these alcohols on benzamide is represented by the two following equations, the first of which represents only a small part of the reaction in the case of the alcohols studied. However, when acid is present to neutralize the ammonia, the first equation represents the total action that takes place.

(1) $C_6H_5CO.NHH + H.OC_2H_5 \rightleftarrows C_6H_5COOC_2H_5 + NH_3$.

(2) $C_6H_5CONH.H + HO.C_2H_5 \rightleftarrows C_6H_5CONHC_2H_5 + H_2O$.

The present work shows that the final result is represented thus but the course of the reactions may not be so simple.

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[Contributions from the Chemical Laboratory of Harvard College.]

CURCUMIN.

By C. Loring Jackson and Latham Clarke.

This paper contains the final account of our work[1] on curcumin—the yellow coloring matter of turmeric. The manuscript was essentially finished early in the summer but was not sent to the press because one of our observations needed to be tested by further experimental work: in the meantime, the paper[2] on curcumin by Milobedzka, von Kostanecki and Lampe reached us, in which they give reasons for adopting the formula $C_{21}H_{20}O_6$, proposed by Ciamician and Silber,[3] in place of ours, $C_{14}H_{14}O_4$. After examining carefully the arguments for each of these formulas, we have come to the conclusion that they are right, and curcumin has the formula $C_{21}H_{20}O_6$. Our reasons for this decision are given in detail in the Experimental Part. With the abandonment of the formula with 14 atoms of carbon our conclusions in regard to the structure of curcumin are swept away and we are glad that the additional facts, which settled the formula, appeared before we had published our paper, as the waste of time from our incorrect theory is thus confined to ourselves, and does not extend to our readers.

We can confirm the statement of von Kostanecki and his associates that curcumin by gentle oxidation yields ferulic acid, as we obtained it by the action of hydric dioxide, which, we should judge, gives a neater method of preparation than the oxidation by the air in alkaline solution used by them.

Of the observations made by us, the most important for the continuation of the work was that the dimethyl ether of curcumin was obtained pure with a quantitative yield by making it in a shaking machine at ordinary temperatures instead of by heat, as done by Ciamician and Silber, whose product was principally viscous with only a very small yield of the crystalline ether. We found the melting point 137°

[1] This Journal, **39**, 696 (1908).
[2] Ber. d. chem. Ges., **43**, 2163 (1910).
[3] Gazz. chim. ital., **27**, I, 561 (1897).

instead of 135°, as given by them. A crystalline substance was also formed in this way from hydroxylamine hydrochloride and curcumin, and it is probable, therefore, that the extremely undesirable products frequently given by curcumin are due to its great sensitiveness to heat when in presence of a solvent.

It is a familiar observation that strong hydrochloric acid turns curcumin brown; we have traced this to the formation of an addition product which was dark brown when little hydrochloric acid gas was used, but turned dull violet with an excess. It was very unstable, decomposing quickly on exposure to the air, and instantly when dropped into water, curcumin being formed. We did not succeed in getting a good analysis of it; but hydrobromic acid formed a similar compound, which was a little more stable, and from this we got a result which came as near to $C_{21}H_{20}O_6(HBr)_3$ as could be expected. Both addition compounds can be kept in corked tubes, which prevents the escape of the acid gas.

It is highly probable that the reddish purple substance formed by the action of phosphoric oxychloride on curcumin[1] is either the addition compound with hydrochloric acid in an impure condition or is a similar substance containing chlorine and phosphorus, as it was converted into curcumin by water in the same way. To be sure it was converted by standing in a desiccator into a black substance instead of curcumin, but this can be ascribed to the further action of the phosphorus compound on the curcumin which was probably the first product of the action.

When curcumin was heated with one of the halogen acids, the methyl haloid was given off at low temperatures, followed, when the heat was raised, by a strongly smelling oily liquid which we could not obtain in large enough quantities to be handled in the usual way. The separation of a few drops of volatile oil from the accompanying acid and the drying of it for an exploratory analysis was a very difficult problem to which we devoted much time, and we thought (it now seems incorrectly) that the composition of this oil would throw much light on the structure of curcumin. Among our many

[1] Jackson and Menke: THIS JOURNAL, **6**, 80 (1884).

attempts to solve this problem, one method which we tried without success, is, we think, worth description here as it may prove of use in other cases. The plan was to dissolve our oil in thiophene or some other liquid containing sulphur, and having in this way raised it to a manageable volume, to wash and dry the mixture in the usual way after which determinations of sulphur and iodine according to Carius would give the data necessary for settling the composition of the new substance. This promising scheme failed with us because we could find no compound containing sulphur which would mix with our product.

The wiping method, by which we finally dried the oil for analysis, has been described in another paper.[1]

EXPERIMENTAL PART.

Ciamician and Silber[2] state that they succeeded in raising the melting point of curcumin to 183° by many crystallizations alternately from methyl alcohol and benzene. Accordingly, we have made a number of attempts to raise it above 178°, the temperature observed by Menke and one of us, by the use of these solvents in the way indicated, and also with glacial acetic acid, and with chloroform, which produces finer crystals than any other solvent we have tried, but in spite of all our efforts, we have never observed a melting point above 178° (uncorr.). We are of the opinion therefore that the difference between the melting point given by Ciamician and Silber and ours is due to a difference in thermometers, and to make certain of the accuracy of the one used by us it was compared with a normal one, and found to differ from it by not more than 0°.2. As the analyses of curcumin made by Ciamician and Silber agree with those of Menke and one of us, it is evident that, if our lower melting point was caused by impurities (which we cannot admit in view of the experiments described above), the amount was not great enough to effect the analyses.

[1] THIS JOURNAL, **44**, 438.

[2] Gazz. chim. ital., **27**, I, 561 (1897).

Formula of Curcumin.

Menke and one of us[1] in 1881 proposed for curcumin the formula $C_{14}H_{14}O_4$, based on the first accurate analyses of the substance and 5 determinations of the constituents of derivatives capable of settling the molecular weight. Ciamician and Silber[2] in 1897 announced that this formula should be replaced by $C_{21}H_{20}O_6$, because two determinations by Zeisel's method of methoxyl in curcumin and one in acetcurcumin gave results in favor of this formula but incompatible with $C_{14}H_{14}O_4$. When we took up the research a few years ago, one of our first undertakings was the study of the application of the Zeisel process to curcumin, when we found that, if the bath stood at 120°, the percentages of methoxyl found (12.31 and 12.69) corresponded to that for one CH_3O group in the formula $C_{14}H_{14}O_4$, which is 12.60; but as the temperature at which the reaction took place was increased, the proportion of argentic iodide found also increased, until at 170° and higher, 16.23 and 16.78 per cents of methoxyl were found, corresponding to the percentage for two (CH_3O) groups in the formula $C_{21}H_{20}O_6$, which is 16.85. As any volatile compound containing iodine would give argentic iodide under the Zeisel conditions, we next studied the nature of the volatile products formed by the action of hydriodic acid on curcumin. For this purpose they were collected instead of being decomposed with argentic nitrate as in the Zeisel determinations, when it was found that the substance given off at 120° had the smell of pure methyl iodide and that it was this substance is shown by the following analysis of this product dried by wiping it with moist filter paper in the way explained in an earlier paper.[3]

0.2102 gram of substance gave 0.3454 gram AgI.

	Calculated for CH_3I.	Found.
I	89.43	88.84

When, however, the process was carried on at 130°, the odor of methyl iodide was distinctly modified by that of a

[1] This Journal, **4**, 77 (1882).
[2] Gazz. chim. ital., **27**, I. 561 (1897).
[3] This Journal, **44**, 438.

different substance with a sharp disagreeable smell, while at 170° to 180° the amount of this new product became sufficient for its odor to mask that of the methyl iodide completely. It was evident, therefore, that the removal of the methyl ran smoothly only at 120°, and that at higher temperatures it was accompanied, or followed, by a deeper decomposition of the curcumin, which formed a second volatile product. As we supposed this was an iodide different from methyl iodide, we inferred that the Zeisel determinations could not be used in support of any formula, and that our work had destroyed the 3 real arguments in favor of $C_{21}H_{20}O_6$, and added 2 to the analytical results which agree with the formula $C_{14}H_{14}O_4$, but are incompatible with $C_{21}H_{20}O_6$. These with our later analyses of derivatives of curcumin and rosocyanin raised the number of arguments in favor of $C_{14}H_{14}O_4$ to 14, while there were none on the other side that seemed to us worthy of use except as confirmatory arguments. We felt justified, therefore, in considering the accuracy of our formula proved.[1] The paper by Milobedzka, von Kostanecki and Lampe[2], however, contained 9 determinations in harmony with $C_{21}H_{20}O_6$ and incompatible with $C_{14}H_{14}O_4$, and although the latter formula still has the advantage, if only the number of determinations is considered, the case is very different when their quality is brought into the discussion, for we can discover no flaw in those given by von Kostanecki and his associates whereas a more careful scanning of ours shows that not one is above suspicion. Thus the 4 determinations of potassium in favor of $C_{14}H_{13}O_4K$ were made on salts prepared by boiling a solution of curcumin or rosocyanin in absolute alcohol with potassic carbonate, and it is possible that enough potassic carbonate might have dissolved in each case to raise the percentage from the 9.63 required by $C_{21}H_{19}O_6K$ to the 13.76 for $C_{14}H_{13}O_4K$. We ought, of course, to have tested this point by experiment, but in this and other cases we were thrown off our guard by the fact that all the determinations made agreed with each other and the theory.

[1] Ber. d. chem. Ges., **38**, 2712 (1905), **39**, 2269 (1906).
[2] *Ibid.*, **43**, 2163 (1910).

The molecular weight determinations were made by the boiling-point method, and subsequent work in another field developed the fact that the conditions then in use by us were so unfavorable that no confidence could be placed in the results. The *p*-brombenzyl compound did not give a perfectly sharp melting point (76°–78°), and this may have been due to the presence of impurities in spite of the chemical purification to which it had been submitted. Finally, in the Zeisel determinations part of the methoxyl may have remained undecomposed at 120°, and the strong smelling oil given off from 120° to 160° may have been, not a new iodide as we supposed, but methyl iodide mixed with a small amount of a product containing no iodine. It is certainly strange, however, that at the temperature at which pure methyl iodide was given off, the amount corresponded to two CH_3O groups in $C_{14}H_{14}O_4$, and that the carbon, hydrogen and bromine in the *p*-brombenzyl compound also agreed with a C_{14} formula.

We have tried in this way to clear away the possible mistakes we have introduced into the chemical literature, and, while we regret them exceedingly, we feel there is some excuse for having been misled by *fourteen* coincidences.

Attention may be called here to two arguments in favor of the formula $C_{21}H_{20}O_6$. The determinations of hydrogen in curcumin (mean 5.63) come out as a rule too low for the value calculated for $C_{14}H_{14}O_4$—5.69—but in harmony with that for $C_{21}H_{20}O_6$—5.43; and the same is true of many of its derivatives. Some preliminary work on the action of hydroxylamine hydrochloride on curcumin gave a compound melting at 162°, which contained carbon 66.04, hydrogen 4.22, nitrogen 3.8, agreeing with the values for $C_{21}H_{21}O_6N$, carbon 65.80, hydrogen 5.48, nitrogen 3.66. We, however, consider our work on this substance so incomplete that these results should not be accepted until they have been tested by further experiments.

Behavior of Curcumin with Halogen Acids.

It is a familiar observation that strong hydrochloric acid turns turmeric paper brown. To study this phenomenon,

some strong hydrochloric acid was added to curcumin, and the brown product washed with water, when curcumin was produced again, as shown by the reappearance of the yellow color and by the melting point 178°. Since this pointed to an addition-product destroyed by water, we next passed gaseous hydrochloric acid, dried with sulphuric acid, over finely powdered curcumin, when the yellow color of the solid changed at once to a characteristic dark brown, which later passed into a dull violet. Upon exposure of this violet product to the air it lost hydrochloric acid rapidly, passing back to curcumin. This change was practically complete in half an hour, although some color lingered for several days. If, on the other hand, the substance was kept in a corked tube, from which the hydrochloric acid could not escape, it retained its color indefinitely. Our attempts to analyze this compound by treating a weighed quantity with water gave poor results, partly on account of the rapid decomposition of the substance, and partly because our products always contained some unaltered curcumin. Passing hydrochloric acid gas into an absolute alcohol or benzene solution of curcumin gave apparently the same substance, but in no more manageable condition. It dissolves in absolute alcohol with a violet color, but this is very fugitive.

In the hope of obtaining a more stable addition compound, dry hydrobromic acid was passed over curcumin. The gas was made by the action of bromine on red phosphorus and water, passed through a tube containing moist red phosphorus to remove any free bromine, and then dried by phosphoric anhydride. The curcumin was powdered as finely as possible and the flask containing it shaken from time to time to expose the whole of it to the action of the hydrobromic acid. The curcumin changed from yellow to brown almost at the instant at which it came in contact with the acid, and this brown color was gradually converted by further action to a blackish violet. After the hydrobromic acid had acted for half an hour, some of the dark violet product was exposed to the air, when it lost the hydrobromic acid mechanically absorbed by the powder, whereas that chemically combined with the

curcumin was given off slowly in dry air or a desiccator, but after long standing in the air all the hydrobromic acid was evolved, leaving curcumin, identified by its yellow color and melting point, 178°; while the same change took place more rapidly *in vacuo*. It follows from this observation that the substance is an addition compound and not formed by substitution. After it had been freed from adhering hydrobromic acid by short exposure to the air, it was analyzed by dropping a weighed quantity of it into water, which decomposed it at once. The curcumin was then filtered out, and the amount of hydrobromic acid in the filtrate determined.

0.3204 gram of substance gave 0.2692 gram AgBr.

	Calculated for $C_{21}H_{20}O_6.3HBr$.	Found.
Br	39.28	35.77

No much better result was to be expected since the substance undoubtedly lost some of the combined hydrobromic acid during its exposure to the air to free it from adhering acid, and it was made from solid curcumin, the parts of which protected by the layer of addition compound might have escaped the action of the hydrobromic acid. That the substance contained 3 or more molecules of hydrobromic acid seems to us established, as the amount of bromine found could not have been higher than that calculated, and $C_{21}H_{20}O_6.2HBr$ contains 30.18 per cent. bromine.

The dark violet substance decomposed slowly in dry air, more rapidly *in vacuo*, or when heated, forming curcumin and hydrobromic acid. The same change was produced instantly by water.

When curcumin was heated in an oil bath at 180°–200° with strong commercial hydrochloric acid, or with a distilled solution of hydrobromic acid, or hydriodic acid, a volatile oil was given off in addition to the methyl haloid but in such small quantity that it was impossible to determine its nature. It had a strong disagreeable smell, was oxidized by potassic permanganate, and decomposed on exposure to the air, turning green.

The black residue left after the action of the acid seemed to be the same in all three cases; in spite of its unpromising properties it was studied by us with the following results. When at first obtained, it was a black tarry mass, and as all attempts to crystallize it failed, it was purified by a method which had given good results with rosocyanin. For this purpose it was first extracted with ether which removed a brown substance, then the black insoluble residue was dissolved in a little alcohol and precipitated with water containing one per cent. of salt. After repeating these processes several times, the powder was washed free from salt, when it contained no halogen and melted at about 200°. It was dried at 100° for analysis.

I. 0.1297 gram of substance gave 0.3383 gram CO_2 and 0.0529 gram H_2O.

II. 0.2064 gram of substance gave 0.5441 gram CO_2 and 0.1029 gram H_2O.

	Calculated for $C_{69}H_{49}O_{17}$.	Found. I.	II.
C	72.06	72.13	71.89
H	4.27	4.60	5.54

The black substance was converted into a potassium salt by adding to its moderately strong alcoholic solution a slight excess of potassic hydrate also dissolved in alcohol, when the black salt was precipitated. It was washed with very little alcohol, and then with ether, and dried in the desicccator.

0.1857 gram of salt gave 0.0794 gram K_2SO_4.

	Calculated for $C_{69}H_{48}O_{17}K_2$.	Found.
K	19.34	18.21

The formula given above agrees with the analytical results better than any other we have found but it would be absurd to claim it is established as no proof can be given that the specimens analyzed were pure, and in a substance with so high a molecular weight a difference of several atoms of carbon makes a change in the percentages which hardly exceeds the limit of experimental error, so that it is not hard

to find other formulas which agree with the analyses; for instance, $C_{72}H_{56}O_{18}$ gives carbon 71.52, hydrogen, 4.63, and $C_{72}H_{49}O_{18}K_7$ gives potassium 18.56. It was an amorphous black powder melting at about 200°, soluble in methyl or ethyl alcohol, or acetone, insoluble in ether, chloroform, benzene, or toluene. It dissolved in strong sulphuric acid with a violet-red color; in a solution of sodic hydrate with a greenish brown color.

Dimethyl Ether of Curcumin, $C_{21}H_{18}(CH_3)_2O_6$.—Ciamician and Silber[1] by heating curcumin, potassic hydrate, methyl iodide and methyl alcohol on the water bath in a flask with a return condenser and a mercury valve, obtained a viscous mass, from which they succeeded in isolating a very small amount of a crystalline product, melting at 135° and giving on analysis, results agreeing with those for the dimethyl ether. In the hope of getting a better yield we carried on the reaction in the cold by placing the mixture in the shaking machine for 16 hours, after which it was allowed to stand at ordinary temperatures for three days. When in this way the reaction took place below 20°, orange yellow crystals 0.5 cm. long were formed, which melted at 137°, and subsequent crystallizations from methyl alcohol showed that this melting point is constant. This modification of the process, therefore, gives a pure compound at once with essentially a quantitative yield.

The dimethyl ether crystallizes in long orange yellow needles, melts at 137° instead of 135° as given by Ciamician and Silber, and in addition to the solubilities given by them is soluble in chloroform or acetone. With a drop of phosphoric oxychloride it turns deep bluish purple.

Action of Hydroxylamine on Curcumin.—As the use of the shaker had given such a good result with the dimethyl ether, we also tried the reaction of the hydrochloride of hydroxylamine in alcoholic solution with curcumin on the shaking machine and found that under these conditions a reaction took place but it ran so slowly that 3 months' shaking was necessary to complete it. Its progress was

[1] Gazz. chim. ital., **27**, I, 561 (1897).

traced by testing from time to time with sodic hydrate, which gave a brown color with curcumin but not with the product of this reaction. The yellow product was purified by crystallization from alcohol.

0.1736 gram of substance gave 0.4204 gram CO_2 and 0.0660 gram H_2O.

	Calculated for $C_{21}H_{21}O_6N$.	Found.
C	65.80	66.04
H	5.48	4.22
N	3.86	3.8

Our results, therefore, agree with those calculated for the monoxime but, as our work did not advance beyond the preliminary stage, they should not be accepted without further experimental tests. The substance formed thick orange-yellow needles melting at 162°, which dissolved in sodic hydrate with a yellow color, but were unaffected by an aqueous solution of sodic carbonate. If an alcoholic solution of curcumin was heated on the steam bath with hydroxylamine hydrochloride for an hour or more, a yellowish white product was formed, which from its melting point, 163°, crystalline form, and the following analysis may be identical with the preceding in spite of the difference in color.

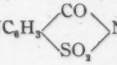
0.2381 gram of substance gave 6.4 cc. N_2 at 20° and 766 mm.

	Calculated for $C_{21}H_{21}O_6N$.	Found.
N	3.86	3.09

The isoxazole obtained by Ciamician and Silber under similar conditions is evidently different from our product as it melted at 173° and contained 69.15 per cent. of carbon.

A STUDY OF ORTHOAMINOPARASULPHOBENZOIC ACID WITH SPECIAL REFERENCE TO ITS FLUORESCENCE.

By J. H. Kastle.

Sometime ago my attention was directed to *p*-aminobenzoic sulphinide, *p*-$H_2NC_6H_3$  NH, as a substance suitable

for the preparation of screens for revealing the presence of ultraviolet light. As is well known, aqueous solutions of this compound exhibit a bluish purple fluorescence in ordinary white light. When some of this substance, moistened with water, was placed in the path of the ultraviolet rays from an iron arc, it was observed to exhibit a beautiful bluish purple fluorescence.[1] If, however, *p*-aminobenzoic sulphinide is moistened with concentrated hydrochloric acid, instead of water, no fluorescence is observed when the mixture is brought into the path of the ultraviolet rays. In solution in concentrated hydrochloric acid this compound also shows no fluorescence in ordinary light. One would naturally imagine, I think, that the destruction of the characteristic fluorescence of this compound by means of hydrochloric acid is associated in some way with the formation of a hydrochloride, the ions of which are no longer fluorescent. The fact that the substance contains an amino group serves, of course, to strengthen such a supposition. On the other hand no hydrochloride of *p*-aminobenzoic sulphinide has ever been isolated and thus far I have been unable to obtain such a compound. The matter is further complicated by the fact that the aminobenzoic sulphinide contains an imino group which might, of course, be altered in such a way by the hydrochloric acid as to involve a change in the physical and chemical properties of the compound, among them its power to fluoresce. There are, therefore, considerable difficulties involved in the way of determining precisely why solutions of this compound lose their power to fluoresce in the presence of hydrochloric acid. About the time that these difficulties came to be recognized, I happened, in the

[1] *The After-glow of Benzoic Sulphinide in Ultraviolet Light.*—The striking fluorescence of *p*-aminobenzoic sulphinide in ultraviolet light naturally led me to test the conduct, in the path of these rays, of such other sulphinides as I happened to have on hand. So far as I was able to observe *p*-nitrobenzoic sulphinide showed no fluorescence and neither did the parent substance, benzoic sulphinide, but after exposure to ultraviolet light the latter compound became luminescent and continued to shine with a pale whitish light for some time after the source of the ultraviolet light had been cut off. In this connection may be mentioned the fact that crystals of benzoic sulphinide emit light when crushed. So far as I am aware, however, its peculiar conduct in ultraviolet light has never been observed prior to this time, and I hope when the opportunity presents itself to make a more thorough investigation of this phenomenon and also of the conduct of other sulphinides in ultraviolet light.

course of my reading, to note that, according to Hart,[1] *o*-amino-*p*-sulphobenzoic acid and its barium salt exhibit a strong blue fluorescence in their aqueous solutions. It, therefore, occurred to me that by reason of its simpler constitution, this compound would perhaps afford a better starting point in the attempt to determine the influence of simple chemical changes on fluorescence.

o-Amino-p-sulphobenzoic Acid, $C_6H_3\begin{cases}COOH\\NH_2(o)\\SO_2OH(p)\end{cases}+0.5H_2O$.—In the preparation of this acid, Hart's general directions were carefully followed with the exception that in the oxidation of the potassium salt of *o*-nitrotoluenesulphonic acid by alkaline permanganate the required amount of the potassium permanganate was added all at once, instead of in small quantities at a time as recommended by Hart. In other words, in the oxidation of potassium *o*-nitrotoluenesulphonate I found it convenient to follow a method which I had previously employed in the oxidation of potassium *p*-nitrotoluenesulphonate. According to this, 10 parts by weight of the potassium salt of *o*-nitrotoluenesulphonic acid, and 3 parts by weight of solid potassium hydroxide are dissolved in 500 cc. of water and to this solution 22 parts, by weight, of finely powdered permanganate are added. The mixture is then heated on a water bath for 8 to 10 hours with occasional shaking. At the end of this time a small quantity of alcohol is added to destroy the excess of permanganate and the mixture filtered to remove the hydrated oxide of manganese. The clear, golden yellow filtrate is then evaporated to small bulk and strongly acidified with concentrated hydrochloric acid. In this way a good yield of the acid potassium salt of *o*-nitro-*p*-sulphobenzoic acid, $C_6H_3\begin{cases}COOH\\NO_2(o)\\SO_2OK(p)\end{cases}$, is obtained. This is then dissolved in strong ammonia and reduced with hydrogen sulphide, in the manner described by Hart, and evaporated to dryness. The residue is then extracted with

[1] THIS JOURNAL, **1**, 354 (1880).

small amounts of warm water and filtered in order to remove the sulphur. The filtrate is then acidified strongly with hydrochloric acid, when the amino acid separates in crystalline condition. As described by Hart, it crystallizes in beautiful rhombic plates of a yellowish color. This yellowish color has been found to be due to impurities, since after several recrystallizations of the acid from water, containing small amounts of animal charcoal, I have obtained it in perfectly colorless condition. One would also be inclined to believe from Hart's description that the acid is anhydrous, whereas, as a matter of fact, it contains one half of a molecule of water of crystallization. That such is the case was first brought to my notice by reason of the fact that 0.217 gram of the air-dried acid required only *19.15* cc. 0.1 N sodium hydroxide for neutralization, whereas, if it were anhydrous, this quantity of the acid should actually require *20* cc. On the other hand, if the acid contains half a molecule of water it has a molecular weight of 226 instead of 217, and, hence, 0.217 gram of the air-dried acid would require only 19.19 cc. 0.1 N caustic soda. In order to determine, therefore, whether the acid is hydrated 0.1511 gram was heated in the air bath at 160° for 1 hour. It lost 0.0063 gram, or 4.16 per cent. Heated for another hour at 160°, the acid showed no further loss of weight. The calculated loss for $H_2NC_6H_3\begin{matrix}COOH\\SO_2OH\end{matrix}$ + 0.5 H_2O is 0.0060 gram, or 3.98 per cent. Of a sample of the acid which had been previously heated to constant weight at 150° to 170°, 0.217 gram required 19.95 cc. 0.1 N sodium hydroxide; calculated, 20 cc. *o*-Amino-*p*-sulphobenzoic acid, therefore, contains half a molecule of water of crystallization. When the hydrated acid is heated in a melting-point tube to 240°, it darkens somewhat but fails to melt at 250°. According to Hart, dilute solutions of *o*-amino-*p*-sulphobenzoic acid and its barium salt show a beautiful blue fluorescence. As compared with sulphate of quinine and aesculin, the fluorescence both of this acid and of the aminobenzoic sulphinide is more of a rich bluish purple than a pure blue. This fluor-

escence is by no means confined to solutions of the free acid and its barium salt but, as one would naturally expect, is probably shown by dilute solutions of all salts of the acid, certainly by all which have been examined up to this time, *viz.*, by the sodium, potassium, ammonium, calcium, barium, lead, magnesium, zinc, manganese, and silver salts. It seems reasonably safe to conclude, therefore, that all of the salts of this acid with a colorless base show a bluish purple fluorescence at great dilutions.

It is also interesting to note in this connection that in ordinary white light, at least, the intensity of the fluorescence of *o*-amino-*p*-sulphobenzoic acid is, within wide limits, inversely proportional to the concentration of its aqueous solutions.

Thus a solution containing 15.48 grams of the acid per liter was found to exhibit, in diffused light at ordinary room temperature, only a slight fluorescence which was by no means comparable in intensity with that of a solution containing only 0.01548 gram per liter. In other words, a solution containing 0.01548 gram of the acid per liter exhibits a far more intense fluorescence than a solution containing a thousand times this quantity of the substance. It has also been found that a 0.001 gram-molecular solution of the acid is decidedly more fluorescent than a 0.01 gram-molecular solution. On the other hand, while a 0.0001 gram-molecular solution of the acid still exhibited a perceptible fluorescence it was decidedly less fluorescent than a 0.001 gram-molecular solution, indicating that there is a limit to the increase in fluorescence by dilution.

The effect of dilution on the intensity of the fluorescence of this compound is so marked, however, that the best way to exhibit its fluorescence in diffused daylight is to drop a few drops of a saturated solution of the acid into a large volume of water, when the path of the more concentrated solution is marked by a very deep and vivid bluish purple fluorescence. It has been observed also that heat diminishes the intensity of the fluorescence of solutions of *o*-amino-*p*-sulphobenzoic acid and its salts.

The fact that the fluorescence of *p*-aminobenzoic sulphinide in ultraviolet light is destroyed by concentrated hydrochloric acid naturally led me to study the effect of strong acids and alkalies on the fluorescence of *o*-amino-*p*-sulphobenzoic acid. This effect is shown in the following series of experiments: A solution (*1*) was prepared containing 0.0226 gram of the *o*-amino-*p*-sulphobenzoic acid in 50 cc. of water. Four tubes were then prepared containing 2 cc. of solution (*1*) and 1 cc. of water or a solution of acid or alkali. The intensity of the fluorescence of these several solutions was then determined by direct comparison with one another, with results as indicated below.

No. of tubes.	Substance.	Intensity of fluorescence.
1	1 cc. water	Strong bluish purple fluorescence
2	1 cc. 1 N hydrochloric acid	Colorless, without fluorescence
3	1 cc. 1 N sodium hydroxide	Colorless, without fluorescence
4	3 cc. water	Colorless, without fluorescence[1]
5	1 cc. 1 N acetic acid	Strong bluish purple fluorescence

In another series of observations, 2 cc. of a 0.01 gram-molecular solution of the amino acid was employed with water, hydrochloric, oxalic, *p*-nitrotoluenesulphonic and acetic acids. The following results were obtained.

No. of tubes	Substance.	Intensity of fluorescence.
1	1 cc. water	Strong bluish purple fluorescence
2	1 cc. 1 N hydrochloric acid	Colorless, no fluorescence
3	1 cc. 1 N oxalic acid	Very slightly fluorescent
4	1 cc. 1 N acetic acid	Strong bluish purple fluorescence
5	1 cc. 1 N nitrotoluenesulphonic acid	Colorless, no fluorescence
6	0.1 cc. 1 N hydrochloric acid	Fluorescent, less than (1)
7	0.1 cc. 1 N oxalic acid	More fluorescent than (6)

[1] Tube 4 contained only distilled water for purposes of comparison.

In another series of experiments, 2 cc. of a 0.01 gram-molecular solution of the amino acid were brought together with 2 cc. of the solutions indicated below and the mixed solutions made up to a total volume of 25 cc. with distilled water. They were then compared as to fluorescence with the following results:

No. of tubes.	Substance.	Intensity of fluorescence.
1	2 cc. water	Strongly fluorescent
2	2 cc. cane sugar (gram-molecular)	Strongly fluorescent
3	2 cc. sodium chloride (gram-molecular)	Strongly fluorescent
4	2 cc. hydrochloric acid (gram-molecular)	Only trace of fluorescence

It is evident, therefore, that the fluorescence of aqueous solutions of *o*-amino-*p*-sulphobenzoic acid is destroyed by strong acids and alkalies—the power to effect this change being roughly proportioned, at least, to the degree of ionization of the acid or base. That the depression of the fluorescence is due to hydrogen and hydroxyl ions is indicated by the fact that cane sugar and common salt have no influence on the intensity of the fluorescence exhibited by such solutions. The intensity of the fluorescence of dilute solutions of the amino acid has also been found to depend on the concentration of all of the substances concerned; for example, if a solution containing 2 cc. 0.01 gram-molecular amino acid and 1 cc. 1 N hydrochloric acid at a total dilution of 3 cc., and which is not fluorescent, is largely diluted with water, the solution again becomes fluorescent and more hydrochloric acid must be added in order to destroy the fluorescence. The effect of dilution on the power of hydrochloric acid to depress the fluorescence of aqueous solutions of the amino acid is shown by the results of the following observations:

Five tubes were prepared and numbered (1), (2), (3), (4) and (5). All contained 2 cc. 0.01 gram-molecular amino acid, in addition to which (1) contained 2 cc. of water, (2) 2 cc. 0.01 N, (3) 2 cc. 0.1 N, (4) 2 cc. 1 N hydrochloric acid, and

(5) 2 cc. 1 N acetic acid. Tubes (1) and (5) showed a strong purplish blue fluorescence, tube (4) only a trace of fluorescence, and tubes (2) and (3) a diminished fluorescence as compared with (1), the diminution being greater in (3) than in (2). In other words, the intensity of fluorescence in these tubes decreased in the order (5) = (1) > (2) > (3) > (4). In still another set of observations, intended to show the effect of hydrochloric acid and also that of dilution on the fluorescence, a set of tubes was prepared and numbered the same as in the above series, the only difference being that the total volume in each case was made up to 25 cc. with distilled water. In this series of observations (1) was found to be strongly fluorescent, (2) less fluorescent than (1), (3) less fluorescent than (1) and (2), and (4) only slightly fluorescent, less than any of the other tubes. In this series of experiments (4) was more strongly fluorescent than (4) in the former series and yet the same amounts of amino acid and hydrochloric acid were present in both, the difference being that the concentration of the two substances had been decreased 6.25 times in the last set of observations. In other words the actual concentration of the hydrochloric acid in (4) in the former series of observations was 0.5 N, whereas in the last series it was 0.08 N.

The effect of sodium hydroxide on the fluorescence of the amino acid is shown in the following table.

No. of tubes.	Amino acid (0.01 gram-molecular).	Other substances.	Degree of fluorescence.
1	2 cc.	23 cc. water	Strongly fluorescent
2	2 cc.	2 cc. 0.01 N NaOH	Slightly less than (1)
3	2 cc.	2 cc. 0.02 N NaOH	Distinctly less than (1) or (2)
4	2 cc.	2 cc. 0.1 N NaOH	Much less than (3)
5	2 cc.	2 cc. 1 N NaOH	Trace of fluorescence, less than (1), (2), (3) or (4)
6	None	25 cc. water	No fluorescence

Total volume in all tubes, 25 cc.

The effect of weak alkali in diminishing the intensity of the fluorescence of aqueous solutions of the amino acid is shown to best advantage at great dilutions. Thus, in a series

of tubes containing the same quantities of amino acid and sodium hydroxide as in the foregoing, but at a total dilution of 100 cc., a very marked diminution in the degree of fluorescence was caused by 2 cc. of 0.02 and 0.01 N caustic soda. At the greater dilution (100 cc.), however, more sodium hydroxide is required to cause the complete disappearance of the fluorescence than at the greater concentration, *viz.*, 25 cc. This is due to the fact, already pointed out, that within very wide limits the intensity of the fluorescence of aqueous solutions of the amino acid increases with dilution. Whether, therefore, a solution of the amino acid will fluoresce in the presence of hydrochloric acid or sodium hydroxide depends on the degree of dilution of the amino acid and on the concentration of the hydrogen or hydroxyl ions. The diminution in the concentration of the hydrogen ions, resulting from the dilution of aqueous solutions of the amino acid, may also enable us to explain the increase in fluorescence resulting from increasing the dilution of aqueous solutions of the acid.

The degree of fluorescence of the normal and acid salts of the amino acid have been compared with that of the acid itself, using 2 cc. of a 0.01 gram-molecular solution of the acid and the quantity of base required to form the normal and acid salt, at a total dilution of 4 cc. and 25 cc. In some cases weighed amounts of the amino acid were brought together with the several amounts of carbonate of the metal required to form the mono and di salt of the acid and the resulting solutions diluted to 0.01 gram-molecular. These were then compared with 0.01 gram-molecular solutions of the amino acid at a total dilution of 4 and 25 cc. Without entering into the details of all of these observations, it has been found in the case of the sodium, potassium, ammonium, calcium, barium and magnesium salts that the intensity of the fluorescence is independent of the nature of the base (provided it be colorless) and that solutions of the free amino acid and of the mono or acid salts are decidedly more fluorescent than those of the di or neutral salts. In all cases, also, the fluorescence of solutions of the acid salts was somewhat

more intense than that of solutions of the free acid at the same dilution, although the differences in degree of fluorescence were in no case so marked as those obtaining for the free acid or acid salt and the neutral salts.

The Disilver Salt of o-*Amino*-p-*sulphobenzoic Acid.*—With the view of preparing the di esters of the amino acid the disilver salt has been prepared and studied. In order to prepare it, weighed amounts of the amino acid were neutralized with the calculated amount of sodium carbonate and to the solution thus obtained was added the required amount of silver nitrate, dissolved in a small amount of water. When these operations are carried out at room temperature, the disilver salt is obtained in the form of an amorphous, curdy, light buff-colored precipitate. On gently warming the liquid containing the amorphous silver salt in suspension, the salt dissolves and almost instantly separates from the light brown solution, this time in the form of a distinctly crystalline, granular precipitate, which is considerably less soluble in water than the amorphous form.

Apparently, therefore, the disilver salt of *o*-amino-*p*-sulphobenzoic acid exists in two forms, one amorphous and curdy, the other crystalline. My attention was first drawn to this fact by reason of the following observations.

A weighed quantity of the amino acid was neutralized with sodium carbonate and precipitated with the calculated amount of silver nitrate. The amorphous precipitate thus obtained was at once filtered with the aid of the pump, and the amorphous mass spread out on filter paper to dry. In the course of a few minutes this tolerably dry material had greatly contracted in bulk and at the same time a large amount of mother liquor had exuded from the material, to such an extent, in fact, as to thoroughly wet the paper upon which the salt had been placed to dry. As the result of this change, the silver salt, which at first was perfectly smooth to the touch, had become gritty and when examined in strong light showed the luster and general appearance of a mass of small crystals.

A few additional observations on these two forms of the disilver salt of the amino acid are not without interest. Two

solutions were prepared: (1) 0.226 gram of the hydrated amino acid and 0.106 gram sodium carbonate in 4 cc. of water; and (2) 0.3398 gram silver nitrate in 4 cc. of water. When these solutions were mixed in equal proportions by volume, a light buff-colored, curdy precipitate was formed. This precipitate tended to redissolve when the solutions were thoroughly mixed, and when gently warmed it did dissolve completely. On continuing to heat the solution, however, a heavy, crystalline, sandy-looking material was deposited which, under the microscope, was seen to consist of compact crystals, generally hexagonal in outline, with rounded edges. The large objects in the field of the microscope had the appearance of crystal aggregates. A microscopic slide was prepared by bringing together 1 drop of each of the solutions. Under a low power ($^2/_3$ in. objective) the precipitate had the appearance of a light brownish, translucent or transparent film. Under a higher power ($^1/_6$ in. objective) this film was seen to consist of a mass of very fine, rounded granules in a clearer and more transparent matrix, and of very irregular, much disintegrated and torn, finely granular, slightly brownish masses. After standing overnight, in a moist chamber to prevent evaporation, the amorphous film had disappeared and in its place crystals and crystal aggregates were to be seen. A similar change was noted in the silver salt which had been preserved in small test tubes, under its own mother liquor. At 27°.5,[1] therefore, the amorphous silver salt slowly changes into the crystalline modification and at higher temperatures, 60° to 100°, this change is practicably instantaneous.

It is evident, therefore, from these and many other observations of a similar nature, that the disilver salt of *o*-amino-*p*-sulphobenzoic acid exists in two forms, one amorphous and unstable at temperatures above 27°.5, the other crystalline and stable at 27°.5 and at higher temperatures. The amorphous variety of the silver salt has also been found to be much more soluble in water than the crystalline form.

[1] By 27°.5 is not meant the transition temperature for this substance, but simply that at a temperature of 27°.5 and higher the amorphous variety of the silver salt becomes crystalline. The true transition temperature for these two forms of this silver salt, if such exists, has not as yet been [illegible]ined.

Up to the present it has been found impossible to obtain the amorphous form in dry condition and, hence, no analysis of it has been attempted. There is nothing to indicate, however, that it is anything other than the disilver salt of the acid under consideration. Of the crystalline silver salt 0.1500 gram gave 0.0988 gram AgCl, corresponding to 49.6 per cent. of metallic silver; calculated for $H_2NC_6H_3\begin{matrix}CO_2Ag\\SO_3Ag\end{matrix}$, 50.08 per cent. silver.

The yield of the crystalline form of the disilver salt depends obviously on the amounts of water employed in making up the solutions used in its preparation. The more concentrated the solutions used, the greater the yield of the silver salt. Thus, 5.942 grams of the silver salt were obtained by mixing together two solutions of (1) 5 grams of the anhydrous amino acid and 2.442 grams sodium carbonate in 50 cc. water and (2) 7.83 grams silver nitrate in 50 cc. water; whereas, when solutions (1) and (2) were prepared with half this quantity of water, *viz.*, 25 cc., 9.2 grams of the silver salt was obtained. In the former case the yield was only 60 per cent of the theoretical, whereas in the latter it was 91.7 per cent.

The Esters of o-Amino-p-sulphobenzoic Acid.—We have seen that all of the metallic salts of *o*-amino-*p*-sulphobenzoic acid which have thus far been prepared show the same fluorescence in their aqueous solutions as the acid itself. The question naturally suggests itself what fluorescence, if any, would be exhibited by the esters of this acid? So far as I am aware, there have been no attempts to prepare these compounds. With the view of obtaining the ethyl ester, the action of ethyl iodide on the disilver salt has been studied. It has been found that when ethyl iodide is added to the dry crystalline silver salt in the proportion of two molecular portions of the former to one of the latter, reaction occurs at once and silver iodide is formed with evolution of heat; and that in order to avoid loss of ethyl iodide by volatilization, it is necessary to work in closed vessels or under an inverted condenser. If the silver salt has the constitution

$C_6H_3\begin{cases}COOAg\\NH_2(o)\\SO_2OAg(p)\end{cases}$, one would naturally expect a diethyl ester of the formula $H_2NC_6H_3\begin{cases}COOC_2H_5\\SO_2OC_2H_5\end{cases}$ to be produced when two molecules of ethyl iodide are allowed to react with one molecule of the silver salt and that from this di ester an acid ester, $H_2NC_6H_3\begin{cases}COOC_2H_5\\SO_2OH\end{cases}$, might easily be obtained.[1]

As a matter of fact, however, the principal compound which I have thus far been able to obtain by the action of ethyl iodide on the disilver salt is a substance which, as nearly as I can judge at present, has the constitution $C_6H_3\begin{cases}COOH\\NHC_2H_5\\SO_2OH\end{cases}+H_2O$.

This substance crystallizes from water in beautiful colorless, rhombic crystals, which melt with decomposition at 243°. In addition to this substance I once obtained a compound crystallizing from water in light, sulphur-yellow crystals, melting at 160°, and which was converted into the colorless rhombic compound by boiling its aqueous solution for some time. Unfortunately this substance was not obtained in sufficient amount for analysis. I am inclined to think, however, that it is a diethyl derivative of the amino acid, either the true di ester, $C_6H_3\begin{cases}COOC_2H_5\\NH_2\\SO_2OC_2H_5\end{cases}$, or a compound having the constitution $C_6H_3\begin{cases}COOC_2H_5\\NHC_2H_5\\SO_2OH\end{cases}$.

In the course of my attempts to prepare a true diethyl ester of *o*-amino-*p*-sulphobenzoic acid I have also obtained a barium salt, which seems to have the constitution

[1] For an account of the esters of certain sulphobenzoic acids see Kastle: THIS JOURNAL, **11**, 187–199 (1889).

$$(C_6H_3\begin{cases}COOC_2H_5\\NHC_2H_5\\SO_2O\end{cases})_2Ba + 4H_2O.$$

The Rhombic Acid, $C_6H_3\begin{cases}COOH\\NHC_2H_5\\SO_2OH\end{cases} + H_2O$.—Up to the present, however, the rhombic compound obtained by the action of ethyl iodide on the disilver salt of *o*-amino-*p*-sulphobenzoic acid has chiefly engaged my attention, but even in my study of this substance I have been handicapped by reason of the fact that I have been able to obtain only poor yields of the substance and, hence, have had only small amounts at my disposal. In one experiment on the preparation of the rhombic acid 9 cc. of ethyl iodide were added to 18.5 grams of the dry, crystalline disilver salt and the flask containing these substances was at once connected with a reflux condenser. Reaction took place immediately, but in order to insure its completion the flask containing these substances was heated for an hour on the water bath, at the end of which time the excess of ethyl iodide was distilled off. The residue was then boiled with 50 cc. of water and filtered to remove silver iodide. During the extraction with boiling water it was observed that considerable effervescence occurred, due perhaps to the rapid formation and evaporation of alcohol or ethyl ether resulting from the decomposition of the normal ester. On cooling and on gradually evaporating in the air, the coffee-colored filtrate continued to yield successive crops of the rhombic compound in small amounts. In no case, however, have I been able to obtain anything approaching a theoretical yield of this substance. The rhombic acid was purified by recrystallization from hot water, the best results being obtained by evaporating its aqueous solutions until a few crystals began to appear on the surface of the solution. When such solutions are allowed to cool spontaneously in the air, the compound is obtained in the form of small, colorless crystals, which under the low power of the microscope are seen to consist of perfect rhombs. When shown some of these crystals, under the microscope, one of the chemists here said

that they looked precisely like minute crystals of calcite. When first placed upon the tongue, the compound is almost tasteless. As it dissolves, however, it gives a mildly sour taste. Its aqueous solutions are acid to litmus and alkaline phenolphthalein. Its concentrated aqueous solutions show but little if any fluorescence. Its dilute solutions have a slight yellow color and show a beautiful pure blue fluorescence. On heating in a melting-point tube the compound begins to darken slightly at 206°, and at 243° it melts to a yellowish brown mass, with effervescence and partial decomposition. The compound is certainly a different chemical species from the *o*-amino-*p*-sulphobenzoic acid. On heating for one hour at 120° and for another hour at 140°, 0.3456 gram of the rhombic acid lost 0.0237 gram, or 6.85 per cent.

In a sulphur determination, by Liebig's method, 0.1673 gram of the compound gave 0.1463 gram $BaSO_4$, equivalent to 0.0201 gram of sulphur, or 12.01 per cent.; calculated for

$$C_6H_3\begin{cases}COOH\\NHC_2H_5\\SO_2OH\end{cases} + H_2O;\ H_2O = 6.84;\ S = 12.18.$$

On neutralizing a solution of the rhombic acid with 0.1 N caustic soda, using phenolphthalein as the indicator, 0.1000 gram of the compound required 7.2 cc.; calculated for

$C_6H_3\begin{cases}COOH\\NH.C_2H_5\\SO_2OH\end{cases} + 1H_2O$, if both hydrogen ions are replaced by sodium, 7.6 cc. In another determination, 0.5000 gram of the acid required 37.41 cc. 0.1 N barium hydroxide; calculated for $C_6H_3\begin{cases}COOH\\NH.C_2H_5\\SO_2OH\end{cases} + 1H_2O$, 38.00 cc.

After neutralizing with 0.1 N barium hydroxide, the solution containing the barium salt was evaporated to small bulk and allowed to stand. Under these conditions the barium salt separated in white pearly plates, the crystal form of which was not very well defined. On drying in the air the barium salt was obtained in the form of a pearly, crystalline powder,

which, on analysis, gave the following values for barium and water: 0.2000 gram of the air-dried salt gave on precipitation with sulphuric acid 0.1004 gram $BaSO_4$, equivalent to 0.0591 gram, or 29.55 per cent., Ba; or calculated on the basis of the anhydrous salt, 35.45 per cent. Ba; calculated for $C_6H_3\begin{cases}NHC_2H_5\\COO\\SO_2O\end{cases}Ba.4H_2O$, 30.35 per cent., and for the anhydrous salt, 36.10 per cent. Ba. On heating to 160° to 180° for 3 hours, 0.2009 gram of the salt lost 0.0335 gram in weight, equivalent to 16.67 per cent. of water; calculated for $C_6H_3\begin{cases}NHC_2H_5\\COO\\SO_2O\end{cases}Ba.4H_2O$, 15.90 per cent.

The mass left after heating to 180° was light yellowish brown in color, indicating that some little charring had occurred. This may account for the fact that the loss which the salt sustained on heating is a little more than the calculated for four molecules of water. It was thought at first that perhaps the rhombic acid, melting at 243°, was an acid ester of the formula $C_6H_3\begin{cases}COOC_2H_5\\NH_2\\SO_2OH\end{cases} + H_2O$. In fact, considering its method of preparation and the general tendency on the part of the di esters of the sulphobenzoic acids to form acid esters, everything would point to this formula for the compound. If now, barium hydroxide reacted with this, molecule to molecule, to form a neutral barium salt, it is necessary to suppose that the carboxylic ester part of the compound is instantaneously saponified by the barium hydroxide in the sense of this equation:

$$C_6H_3\begin{cases}COOC_2H_5\\NH_2\\SO_2OH\end{cases} + Ba(OH)_2 = C_6H_3\begin{cases}COO\\NH_2\\SO_2O\end{cases}Ba + C_2H_5OH\ [+H_2O;$$

in which event we should obtain the original *o*-amino-*p*-sulphobenzoic acid by the action of sulphuric acid on the barium salt. On the other hand, on evaporation, the filtrate obtained in the barium determination on this salt yielded

the original rhombic acid from which the barium salt had been prepared by neutralization with barium hydroxide, *viz.*, $C_6H_3\begin{cases}COOH\\NH.C_2H_5\\SO_2OH\end{cases} + H_2O$, as determined by its melting point and other physical characteristics. In the formation of the rhombic acid, therefore, it is necessary to assume a migration of an ethyl group from either the carboxyl or sulphoxyl group to the amino part of the compound or a migration of the silver atoms to the amino part of the compound in the preparation of the disilver salt. In fact, the peculiar behavior of the silver salt in passing from an amorphous to a crystalline form naturally suggests some such molecular rearrangement; and certainly everything that is now known concerning the rhombic acid points to its being the monohydrate of *o*-ethylamino-*p*-sulphobenzoic acid. It is of interest to note in this connection that in his attempts to prepare the dimethyl ester of *p*-amino-*o*-sulphobenzoic acid, by the action of methyl iodide on the silver salt of this acid, Hedrick[1] obtained a dimethylaminosulphobenzoic acid, $C_6H_3\begin{cases}COOH\\N(CH_3)_2(p),\\SO_3OH(o)\end{cases}$ in which the two methyl groups are in combination with the nitrogen. On the other hand, by the action of ethyl iodide on the silver salt of the *p*-aminosulphobenzoic acid and subsequent neutralization of the product with barium carbonate he obtained a barium salt to which he assigned the formula $\left(C_6H_3\begin{cases}COOC_2H_5\\SO_2O\\NH_2\end{cases}\right)_2Ba$. It is evident, therefore, that the esterification of the aminosulphobenzoic acids is a process which will well repay further investigation. This investigation is now under way.

Like the parent acid, the ethyl derivative of *o*-amino-*p*-sulphobenzoic acid is fluorescent in its dilute aqueous solutions. These solutions have a faint yellowish color and ex-

[1] This Journal, **9**, 413–414 (1887).

hibit a strong, pure blue fluorescence, instead of the more purplish-blue fluorescence of the amino acid. In this connection it is interesting to note that in certain instances, at least, the introduction of ethyl groups into red dyestuffs changes their color to blue. The effect of introducing an ethyl group into *o*-amino-*p*-sulphobenzoic acid certainly has the effect of rendering the fluorescence more blue. Like the original amino acid, the ethyl derivative exhibits but little if any fluorescence in concentrated aqueous solutions. At great dilution, however, the fluorescence is very intense. The barium salt of the ethyl acid also shows the same fluorescence as the ethyl acid itself.

Attempts to prepare the benzoyl derivative of *o*-amino-*p*-sulphobenzoic acid have been without success—the only products resulting from the benzoylation being the unchanged amino acid and benzoic acid. These experiments were carried out, however, before I was aware that the amino acid contained water of crystallization and it is more than likely that the presence of water in the compound prevented the formation of the benzoyl derivative.

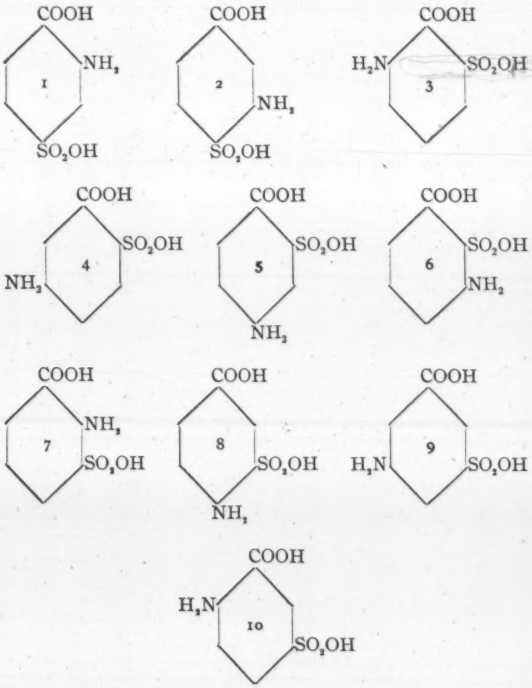
On the other hand, Hedrick[1] also failed to obtain the benzoyl derivative of *p*-amino-*o*-sulphobenzoic acid, which is anhydrous, so that the failure to obtain the benzoyl derivative in the present case may not be due to the presence of water in the molecule, but to some protection afforded the amino group by the other groups present in the molecule. If there is an actual shifting of the silver atoms from the acidic groups of the compound to the nitrogen, then it ought to be possible to obtain the benzoyl derivative by the action of benzoyl chloride on the silver salt. This point will be further investigated.

Attempts to prepare salts of the amino acid of the type of the hydrochloride $C_6H_3\begin{cases}COOH\\NH_2.HCl\\SO_3OH\end{cases}$ have likewise resulted in failure, possibly for the reason that the hydrated amino

[1] *Ibid.*, 414.

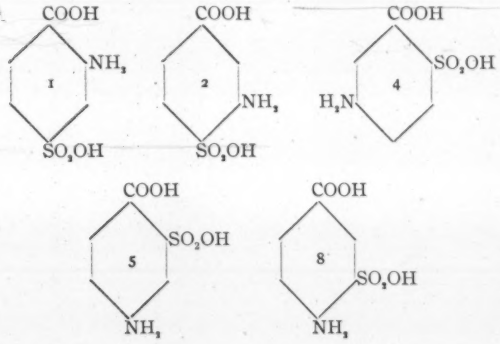
acid was also employed in these experiments. Further efforts will, therefore, be made to obtain salts of the substituted ammonium type by working with the anhydrous acid.

As is well known, there are, according to our present views respecting isomerism in the benzene series, ten isomeric monaminosulphobenzoic acids. These have the following formulas:



According to Richter eight of the compounds given in the

literature as having the composition $C_7H_7O_5NS$ are aminosulphobenzoic acids. So far as I have been able to ascertain, however, and in this search I have been aided by Mr. McDermott of the Hygienic Laboratory, Washington, D. C., to whom my thanks are due, only five are described in the literature at present accessible to me. These are:



It is interesting to note that except in the case of (1) and (2), nothing is said as to the fluorescence of any of these five acids. The compound (1), of course, is the acid here under consideration and is markedly fluorescent. In the case of (2), Hart described the fluorescence of dilute solutions of its barium salt, but makes no mention of the fluorescence of the acid itself. From my own observations on the fluorescence of the *o*-amino-*p*-sulphobenzoic acid, and its salts, it appears more than likely that Hart's acid (2) will itself be found to be fluorescent. It is also certain that in ordinary white light neither the *p*-amino-*o*-sulphobenzoic acid (5) itself nor its salts are fluorescent. It is also interesting to note that in the two aminosulphobenzoic acids in which fluorescence has been observed, *viz.*, (1) and (2), the amino group is in juxtaposition to one of the other groups in the molecule and not further removed than the meta position from the

second acidic group. Furthermore, if Hart's observations are correct, acid (1) is more strongly fluorescent than acid (2). In the former the amino group is ortho to the carboxyl and meta to the sulphonic acid group, whereas in the latter the position of the amino group with respect to the other two groups is reversed. If now the relative position of the amino group with regard to the carboxyl and sulphonic groups in this series of compounds is the sole determining factor in the fluorescence or nonfluorescence of the aminosulphobenzoic acids, then we would expect to find acid (7) to be the most strongly fluorescent of any of these compounds. Acids (3) and (10) would also probably exhibit fluorescence, whereas acids (4), (5), (8) and (9) should exhibit no fluorescence. As a matter of fact, while acids (4), (5) and (8) are all known, nothing has been said by any author to indicate that either of them is fluorescent. Acid (6) presents such peculiarities with regard to the relative position of the amino group with respect to the carboxyl and sulphonic groups that at present nothing can be said as to the probability of its showing fluorescence.

The whole problem of the relation of constitution to fluorescence in the case of these aminosulphobenzoic acids is of great chemical interest and is such as to warrant an exhaustive investigation. Indeed, it would seem that a better idea of the influence of constitution on the phenomenon of fluorescence could be obtained from an intensive study of a comparatively small series of closely-related compounds, such as these aminosulphobenzoic acids, than we could ever hope to obtain from investigations covering such a wide range of chemical substances as are ordinarily included in investigations of this kind. I hope, therefore, to continue this investigation as rapidly as the time at my disposal and the resources of my laboratory will permit.

UNIVERSITY OF VIRGINIA,
October, 1910.

[Contributions from the Sheffield Laboratory of Yale University.]

CLXXXVII.—RESEARCHES ON PURINES: ON AN ISOMER OF XANTHINE; 2,8-DIOXYPURINE.

By Carl O. Johns.

[SECOND PAPER.[1]]

Two of the three isomers of dioxypurine required by theory have been described in chemical literature, namely, xanthine or 2,6-dioxypurine (IV) and 6,8-dioxypurine (VI). The synthesis and properties of 2,8-dioxypurine (V) are described in this paper.

The first known and most inportant of these dioxypurines is xanthine. This compound was described in the year 1817 by Marcet[2] who isolated it from urinary calculi. The structure of xanthine remained unknown for a long time. Medicus[3] proposed the formula of 2,6-dioxypurine (IV) as probably representing its constitution. From the results of his first investigations in this series, Emil Fischer was led to believe that xanthine[4] was 2,8-dioxypurine (V) and this formula was accepted for many years. By his later investigations, Fischer showed that xanthine[5] is 2,6-dioxypurine (IV). Fischer and Ach[6] have prepared 6,8-dioxypurine (VI). This compound is considerably more soluble than xanthine in hot water. Moreover, xanthine gives the murexide reaction while 6,8-dioxypurine does not. The writer has obtained 2,8-dioxypurine (V) by heating a mixture of urea and 2-oxy-5,6-diaminopyrimidine at 180°–190°. This is the method employed by Gabriel and Colman[7] to obtain purines from diaminopyrimidines.

2,8-Dioxypurine resembles xanthine in many respects. It gives a strong murexide reaction. When carbon dioxide

[1] The first paper of this series appeared in This Journal, **41**, 58 (1909).

[2] An Essay on the Chemical History and Medical Treatment of Calcal Disorders. London, 1817.

[3] Ann. Chem. (Liebig), **175**, 230 (1875).

[4] *Ibid.*, (Liebig), **215**, 313 (1882).

[5] Ber. d. chem. Ges., **30**, 549 (1897).

[6] *Ibid.*, Ges., **30**, 2218 (1897).

[7] *Ibid.*, Ges., **34**, 1247 (1901).

is passed into a potassium hydroxide solution of the base, the free base is precipitated. Its hydrochloride is analogous to that of xanthine. Solutions of the base in mineral acids give a precipitate of the free base when poured into water. It is slightly more soluble than xanthine in hot water.

The sodium and potassium salts of 2,8-dioxypurine are but moderately soluble in cold water and are easily prepared. The sodium salt is the most characteristic of the two, forming stout prisms that contain 4 molecules of water. The sodium salt of xanthine contains but 1 molecule of water.

If 2,8-dioxypurine were formed in the hydrolysis of nucleoproteids or nucleic acids, it could easily be mistaken for xanthine. It can be distinguished from xanthine by preparing the sodium salt. This can be done with less than 0.5 gram of the base.

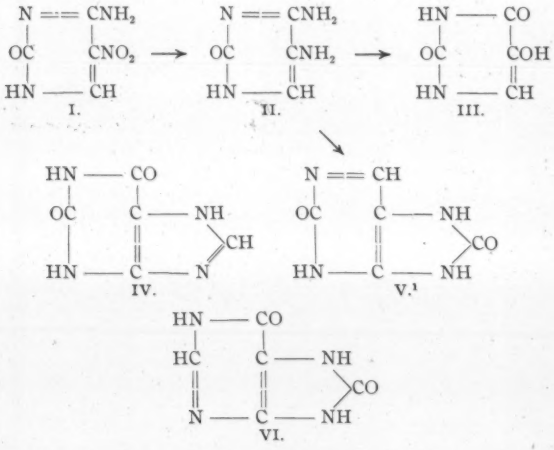
The greatest difficulty encountered in these experiments was in the preparation of 2-oxy-5,6-diaminopyrimidine[1] (II). Attempts to prepare it in quantity by reducing nitrocytosine (I) with aluminium amalgam resulted chiefly in the formation of black decomposition products. After various reducing agents had been tried without success, it was found that the use of ferrous hydroxide gave a yield of more than 60 per cent. of the pure crystallized diaminopyrimidine. It is probable that other nitropyrimidines can be successfully reduced by this method.

2-Oxy-5,6-diaminopyrimidine is more stable than we were led to believe in our former paper.[2] The presence of a large quantity of decomposition products made it appear that the pyrimidine was extremely unstable. Its aqueous solution can be evaporated under atmospheric pressure without marked decomposition. The base has also been found to give well-crystallized salts with mineral acids. The solution which we used in our previous work was probably too dilute as we did not obtain any salts at that time.

When 2-oxy-5,6-diaminopyrimidine is heated in a sealed tube with 20 per cent. sulphuric acid at 140°–150° it is readily converted into isobarbituric acid (III). This makes it im-

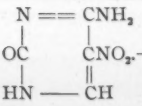
[1] Johnson, Johns and Heyl: THIS JOURNAL, **36**, 170 (1906).
[2] *Loc. cit.*

probable that 2-oxy-5,6-diaminopyrimidine will be found in the hydrolysis of nucleic acids, because if it were formed as a cleavage product it would readily be changed to isobarbituric acid These researches will be continued.

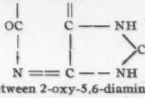


I. II. III. IV. V.[1] VI.

EXPERIMENTAL PART.



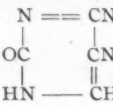
Nitrocytosine,[1] OC CNO_2.—The nitrocytosine used in

[1] The writer has used the formula proposed by Fischer (*Untersuchungen in der Puringruppe*, p. 19) to represent the structure of 2,8-dioxy purine. If written in its tautomeric form this would be  which would, perhaps, show more clearly the relationship between 2-oxy-5,6-diaminopyrimidine (II) and 2,8-dioxypurine.

[2] Wheeler and Johnson: THIS JOURNAL, **31**, 591 (1904). Johnson, Johns and Heyl: *Ibid.*, **36**, 166 (1906).

these experiments was made from synthetic cytosine.[1] A quantitative yield was obtained as follows: Ten grams of dry cytosine were dissolved in 20 cc. of cold concentrated sulphuric acid, and 10 grams of nitric acid (sp. gr. 1.5) were gradually added. Heat was evolved and in some cases it became necessary to cool the mixture. After standing for fifteen minutes the resulting solution was poured into 200 cc. of cold water and the acids were neutralized with ammonia. The nitrocytosine separated rapidly and was filtered off and washed as soon as the mother liquor had become cold. The nitrocytosine thus obtained was almost white.

2-Oxy-5,6-diaminopyrimidine,[2]



$CNH_2.H_2O$.—Eight grams of pulverized nitrocytosine were dissolved in 200 cc. of concentrated ammonia. To this was added a solution of 96 grams of crystallized ferrous sulphate in 300 cc. of water. When the two solutions were mixed there was a marked rise in temperature. When the mixture had stood at room temperature overnight, the sulphuric acid was precipitated by adding a solution of 112 grams of crystallized barium hydroxide in 200 cc. of hot water. The mixture was then heated for a half hour on the steam bath and carbon dioxide was passed in to remove a slight excess of baryta. After filtering the hot solution by suction, the filtrate was evaporated in an open dish on the steam bath until about 100 cc. remained. This was filtered to remove a slight precipitate. Slender, colorless prisms were formed on cooling the filtrate rapidly, but when cooled slowly, stout prisms were obtained, some of which were two cm. long. A small quantity of amorphous material was usually associated with the crystals. This was easily dissolved before filtering by the addition of a few drops of ammonia. The yield of pure hydrous crystals was 65 per cent. of the calculated.

[1] Wheeler and Johnson: THIS JOURNAL, **29**, 498 (1903).
[2] Johnson, Johns and Heyl: *Ibid.*, **38**, 179 (1906).

4.130 grams of substance lost 0.520 gram of H_2O at 120°.
0.5592 gram of substance lost 0.0692 gram of H_2O at 120°.

	Calculated for $C_4H_6ON_4H_2O$.	Found. I.	Found. II.
H_2O	12.50	12.59	12.37
N	38.18	...	38.54

	Calculated for $C_4H_6ON_4$.	Found.
N	44.44	44.05

The diaminopyrimidine was easily soluble in hot and sparingly soluble in cold water. It could be recrystallized without apparent decomposition although its aqueous solution darkened slowly on prolonged boiling.

Action of 20 Per Cent. Sulphuric Acid Heated under Pressure.—One gram of the crystallized diaminopyrimidine was dissolved in 20 cc. of 20 per cent. sulphuric acid and the solution was heated in a sealed tube at 140°–150° for three hours. The tube was cooled overnight. It contained 0.7 gram of precipitate which was composed of small balls of microscopic prisms. These were difficultly soluble in hot water but dissolved easily in dilute ammonia. The aqueous solution reduced an alkaline silver nitrate solution with the formation of a silver mirror. The substance was identified as isobarbituric acid, both amino groups having been substituted by hydroxyl.

	Calculated for $C_4H_4O_3N_2$.	Found.
N	21.87	22.26

The Hydrochloric Acid Salt, $C_4H_6ON_4.2HCl$.—One-half gram of the hydrous diaminopyrimidine was dissolved in 20 cc. of hot 10 per cent. hydrochloric acid. The salt was rather difficultly soluble in the hot acid and separated on cooling, in plates that formed laminated clusters. These did not lose weight at 110°.

0.1328 gram of substance gave 0.1911 gram of AgCl.

	Calculated for $C_4H_6ON_4.2HCl$.	Found.
Cl	35.68	35.57

The Sulphuric Acid Salt, $C_4H_6ON_4.H_2SO_4.H_2O$.—One-half gram of the hydrous base was dissolved in 10 cc. of hot 10 per cent. sulphuric acid and the solution was left at room temperature. Stout prisms separated. When cooled rapidly the solution gave needles or slender prisms. The deposit weighed 0.6 gram when dried over sulphuric acid.

0.3997 gram of substance lost 0.0265 gram of H_2O at 110°.

	Calculated for $C_4H_6ON_4.H_2SO_4.H_2O$.	Found.
H_2O	7.43	6.64

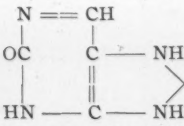
0.1212 gram of anhydrous substance gave 0.1212 gram of $BaSO_4$.

	Calculated for $C_4H_6ON_4.H_2SO_4$.	Found.
S	14.28	13.74

The Nitric Acid Salt, $C_4H_6ON_4.4HNO_3$.—One-half gram of hydrous base was dissolved in 7 cc. of hot 20 per cent. nitric acid. Crystals formed slowly but after standing in a test tube for 2 days the deposit weighed 0.8 gram. The crystals were stout colorless prisms and were anhydrous. They decomposed slowly when heated at 110°. Analyses of the air-dried crystals indicated that they were composed of 1 molecule of base to 4 molecules of nitric acid.

	Calculated for $C_4H_6ON_4.4HNO_3$.	Found. I.	II.	III.
N	29.63	29.02	29.30	29.84

2,8-Dioxypurine,



CO.—Four and six-tenths grams of dried 2-oxy-5,6-diaminopyrimidine were mixed with 5 grams of urea and the mixture was ground to a fine powder in a mortar. This powder was then heated at 180°–190° in an oil bath for a half hour. The powder melted and gave off ammonia, leaving a hard cake. This was treated with hot dilute ammonia and gave a straw-colored solution. A

trace of insoluble substance was filtered off. On acidifying the hot solution with acetic acid, and cooling, 5.1 grams of 2,8-dioxypurine were obtained. This was 92 per cent. of the theoretical yield. The purine was almost insoluble in cold water, and it required about 1100 cc. of boiling water to dissolve 1 gram. When precipitated from a hot ammoniacal solution by acetic acid the purine comes down as a white powder which is composed of extremely small microscopic prisms. When the purine was dissolved in hydrochloric acid to which a crystal of potassium chlorate was added and the resulting solution was evaporated carefully a yellow residue was obtained. When this residue was moistened with ammonia it turned purple, giving the murexide reaction. Analyses of the purine gave the following results:

0.1687 gram of substance gave 0.0437 gram of H_2O and 0.2471 gram of CO_2.

0.1517 gram of substance gave 0.0411 gram of H_2O and 0.2218 gram of CO_2.

	Calculated for $C_5H_4O_2N_4$.	Found. I.	II.
C	39.47	39.95	39.88
H	2.63	2.87	3.00
N	36.84	36.92	...

A solution of the sodium salt in water gave precipitates with silver nitrate, lead acetate, and mercuric chloride. Carbon dioxide precipitated the free base from its potassium hydroxide solution. A solution of the base in mineral acids gave a precipitate of free base when poured into water.

The Nitric Acid Salt, $C_5H_4O_2N_4.2HNO_3$.—This was obtained by dissolving 0.4 gram of 2,8-dioxypurine in 5 cc. of hot 20 per cent. nitric acid. On standing overnight the solution gave a deposit of short, stout prisms. The yield was 0.6 gram or 82 per cent. of the calculated.

	Calculated for $C_5H_4O_2N_4.2HNO_3$.	Found. I.	II.
N	30.21	30.00	30.41

The Hydrochloric Acid Salt, $C_5H_4O_2N_4.HCl$.—When the purine was mixed with hydrochloric acid, a hard crust formed,

rendering the salt rather difficultly soluble. One-half gram of 2,8-dioxypurine was dissolved in 15 cc. of hot concentrated hydrochloric acid and the solution allowed to stand overnight. Small prisms with a lenticular outline separated. These weighed 0.3 gram.

0.1589 gram of substance gave 0.1166 gram of AgCl.

	Calculated for $C_5H_4O_2N_4.HCl$.	Found.
Cl	18.81	18.15

The Potassium Salt, $K.C_5H_3O_2N_4.2H_2O$.—This compound crystallized out rapidly when 0.5 gram of 2,8-dioxypurine was dissolved in 10 cc. of hot normal potassium hydroxide and the solution was cooled. The yield was 0.6 gram, or 80 per cent. of the calculated. The salt formed a bulky mass of needlelike crystals. It contained 2 molecules of water which it lost at 130°, but the anhydrous salt absorbed water slowly from the air until 2 molecules of water had been absorbed.

0.5080 gram of substance lost 0.0785 gram of H_2O at 130°.
0.5037 gram of substance lost 0.0759 gram of H_2O at 130°.
0.1172 gram of anhydrous substance gave 0.0533 gram of K_2SO_4.

	Calculated for $K.C_5H_3O_2N_4.2H_2O$.	Found. I.	Found. II.
H_2O	15.92	15.45	15.07

	Calculated for $K.C_5H_3O_2N_4$.	Found.
K	20.52	20.42

The Sodium Salt, $Na.C_5H_3O_2N_4.4H_2O$.—One-half gram of 2,8-dioxypurine was dissolved in 5 cc. of hot normal sodium hydroxide. After the resulting solution had stood overnight, a compact mass of stout prisms was obtained. These weighed 0.5 gram, or 60 per cent. of the calculated. An attempt was made to dry the salt over sulphuric acid but it lost its luster and part of the water of crystallization. The air-dried salt contained 4 molecules of water.

0.4578 gram of substance lost 0.1320 gram of H_2O at 130°.
0.3825 gram of substance lost 0.1116 gram of H_2O at 130°.
0.1870 gram of anhydrous substance gave 0.0741 gram of Na_2SO_4.

	Calculated for $Na.C_5H_3O_2N_4.4H_2O$.	Found. I.	II.
H_2O	29.26	28.84	29.18

	Calculated for $Na.C_5H_3O_2N_4$.	Found.
Na	13.21	12.85

The Ammonium Salt.—This was obtained as a mass of slender needles when 2,8-dioxypurine was recrystallized from ammonia. It was unstable when dried, losing ammonia rapidly.

NEW HAVEN, CONN.,
November 5, 1910.

REVIEWS.

RADIOCHEMISTRY. By A. T. CAMERON, M. A., B.Sc., Lecturer in Physiological Chemistry, University of Manitoba. London: J. M. Dent and Sons, Ltd. 1910. pp. viii + 174.

The scope of this little volume can be best seen from a few lines taken from the preface. "The title of this book has been chosen deliberately; the science of radioactivity has developed to such an extent as to make it justifiable and convenient to divide it. Here it is treated from a chemical standpoint; the physical side is introduced only so far as is necessary to explain the special experimental methods." The contents are: Historical Introduction; Radioactive Methods Illustrated by the Thorium Series of Elements; the Radiations from Radioactive Elements; Life of a Radioactive Element; Classification of the Radioactive Elements—Their Physical and Chemical Properties; Methods of Work with Radium Emanation and The Life Period of Radium; The Atomic Weight of the Emanations; Liquid and Solid Radium Emanation; the Chemical Effects Produced by the Radiations; The Production of Helium during Radioactive Changes and its Identity with the α Particle; Recent Attempts at Transmutation; Chemical Evidences of Transformation; Recent Results and Speculations; Radiogeology; The Medical Application of the Radiations. The author, having worked in this field to such good purpose with Ramsay, is eminently capable

of dealing with the subject from the standpoint not of the compiler but of the investigator.

No chapters in the book will be read with more interest than those which deal with the transformation and transmutation of the chemical elements and it is interesting to all that the author distinguishes clearly between these two processes. When Ramsay first showed that helium is produced from the radium emanation, it was said, by some, that the dream of the alchemist had been realized, and that transmutation of one chemical element into another had been effected. A moment's thought showed that this was not true. Finding an unstable system in nature which spontaneously broke down, yielding other things, and among them an element, was very different from artificially producing one chemical element from another.

Cameron recognizes, very clearly, this difference and calls the first process "transformation" and the latter "transmutation" of the chemical elements. The work of Ramsay and Cameron on the production of lithium from copper is described in detail, and also the work of Mme. Curie and Mlle. Gleditsch in which negative results were obtained. Cameron sums up the facts thus: "The two series of experiments would appear to have been carried out in a perfectly parallel way; the only explanation that permits them to be homologated is that in those of Ramsay and Cameron, any lithium in the glass was undissolved by copper sulphate solution (as actually shown) unless emanation was present."

H. C. J.

CHEMISCH-OPTISCHE UNTERSUCHUNGEN. Von J. H. JELLETT. Übersetzt von L. FRANCK. Ostwald's Klassiker der Exakten Wissenschaften, No. 163. Herausgegeben von W. NERNST. Mit 6 Figuren im Text. Leipzig: Verlag von Wilhelm Engelmann. 1908. pp. 83. Price, M. 1.60.

This number of the "Klassiker" is a translation of three papers from the Transactions of the Royal Irish Academy. Says Nernst: "This work of Jellett's contains apparently an entirely independent, and in many respects an original, development of the law of mass action, chiefly in its application to chemical statics. Yet, at the same time, the principles of chemical kinetics are clearly explained."

The priority in connection with the fundamental laws of chemical dynamics and equilibrium is usually accredited to the Norwegians, Guldberg and Waage. It seems that the work of Jellett takes its place with that of the above-named investigators. The convenient form and inexpensive character

of the volumes published in "Ostwald's Klassiker" make this work readily accessible to all who are interested in this branch of science. H. C. J

DIE METHODEN DER MASSANALYSE. Zugleich völlig umgearbeitete 8. Auflage von FR. MOHR'S LEHRBUCH DER CHEMISCH-ANALYTISCHEN TITRIERMETHODE. Erste Abteilung. Von DR. H. BECKURTS, ordentlicher Professor und Vorstand der technischen Hochschule, Braunschweig. Unter Mitwirkung von DR. O. LÜNING. Mit 87 eingedruckten Abbildungen. Braunschweig: Vieweg und Sohn. 1910. pp. vii + 482. Price, M. 14.

In a prefatory note, the publishers state that the last edition of Mohr's "Titriermethode" which actually came from his pen was the fifth, published in 1877. Two later editions were issued (the last in 1896), which were revised by Professor Classen, the revision consisting mainly in the introduction of new methods without any extensive recasting of the remaining material. The purpose of the authors of the present edition has been to prepare what is practically a new work, taking Mohr's text-book as a model. They have intended to include all volumetric processes which have been proved to be of practical significance for a particular determination, and to discuss the practical application of each of these. They have, however, omitted material which occupied a considerable portion of Mohr's manual, namely the discussion of the application of volumetric processes in the more or less complete schemes of analysis of natural or artificial products, much of which dealt with gravimetric or gasometric methods not rigidly within the scope of a work on volumetric analysis.

The portion of the manual now published, and under review, includes a general discussion of the methods and apparatus employed in volumetric analysis, and the processes of alkalimetry and acidimetry (with an extended consideration of indicators), and the methods of iodimetry, chlorimetry and bromimetry.

There has been need of an authoritative work dealing with volumetric analysis which should bring the subject up to date. This volume seems to be such a treatise as is called for. The references indicate that the recent literature has received due attention (the text-books will always lag somewhat behind the latest utterances) and the theoretical discussions are modern in character. Any work which attempts to cover so wide a field must serve rather as an index to original sources of information than as an exponent of details. In this case the compilation appears to have been carefully done, and the volume may be heartily commended to the attention of all analysts.

The second division of the work is promised in the near future and its appearance is anticipated with interest.

H. P. TALBOT.

THE CHEMICAL ANALYSIS OF ROCKS. By HENRY S. WASHINGTON, PH.D. Second edition. New York: John Wiley and Sons. 1910. pp. xi + 200. Price, $2.

The new edition differs very little from the first.[1] The book has been somewhat enlarged by the introduction of new methods and by additional detail in the description of some of the older processes. The subject matter has been partly rearranged so that the directions for procedure more nearly parallel the actual laboratory work. The manual should be very useful to the chemist or petrologist with slight analytical training.

R. S. WILLIAMS.

SOILS AND MANURES. By J. ALLAN MURRAY, B.Sc. New York: D. Van Nostrand Company. pp. xiii + 354. Price, $2.00

This book deals with the origin, physical properties, chemistry and biology of soils, the principles of manuring and the various sources of plant food. It is of value to the student who desires to secure information concerning the principles of manure and soil fertility from the English point of view. It cannot, however, be recommended to those who are seeking information concerning American soils or American fertilizing practices. Matters of importance to an American are hardly mentioned and many things are discussed in detail which are of comparatively little importance in this country. Cotton and Indian corn, for example, are hardly mentioned at all. The expression of analyses of mixed fertilizers in terms of phosphates instead of phosphoric acid is not in accordance with our usage. Acid phosphate is extensively mixed with almost all kinds of material in this country and the cautions concerning its mixing and the statement that the only safe rule is not to mix phosphate with anything before applying it to the land appear peculiar to us.

G. S. FRAPS.

[1] THIS JOURNAL, **33**, 435.